

# RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XVIII

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*April, 1945*

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DIVISION OF RUBBER CHEMISTRY  
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# RUBBER CHEMISTRY AND TECHNOLOGY

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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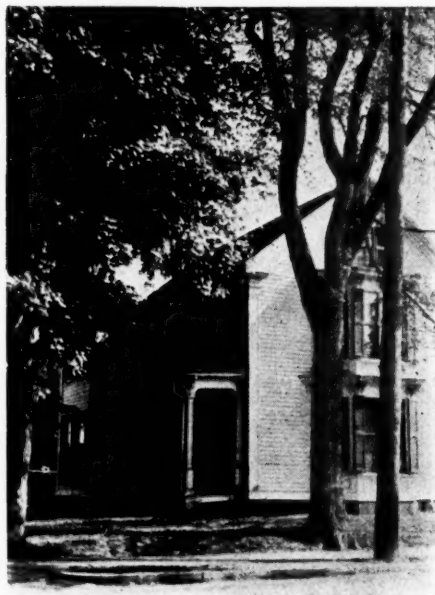
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## A SHRINE OF THE RUBBER INDUSTRY, 1839-1945



*Photograph by C. C. Davis.*



*Photograph by Earle E. Langeland.*

The Goodyear house in Woburn, Massachusetts, where in 1839 Charles Goodyear made his epochal discovery that natural rubber can be vulcanized by sulfur.  
The house still stands essentially unchanged, is privately owned, and is occupied at present.

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### NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1943. (Vol. VII). Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W.1, England.  $7\frac{1}{4} \times 9\frac{3}{4}$  in. 130 pp. Price to Members: 4/6 (approximately \$1.25); Non-Members: 12/6 (approximately \$3.25).—This latest annual report on the progress of world-wide rubber technology is again ably edited by Drakeley and again covers all phases of the rubber industry, with leading experts and technologists contributing specific chapters on developments during 1943. Beginning with a historical and statistical review, the subjects include planting and production of rubber and latex; properties, applications and uses of latex; chemistry and physics of raw rubber and rubber derivatives; synthetic rubber; testing equipment; compounding ingredients; fibers and textiles; chemical and physical properties of vulcanized rubber; tires; belting; hose and tubing; cables and electrical insulation; footwear; mechanical goods; flooring; surgical goods; textile-rubber composites; sponge rubber; hard rubber; works processes and materials; and machinery and appliances. As usual, excellent name and subject indexes, the latter carefully cross-referenced, are included. [From *The Rubber Age* of New York.]

REPORT ON THE OPERATIONS OF RUBBER DEVELOPMENT CORPORATION. By Douglas H. Allen. Issued by Rubber Development Corp., Washington 25, D. C.  $8 \times 10\frac{1}{2}$  in. 22 pp.—This report, submitted by the author on his retirement as president, covers the operations of the Rubber Development Corporation, the government agency charged with the procurement of crude rubber, from February 23, 1943, the date of its formation, to August 31, 1944. It contains data on the amount of rubber acquired, cost per pound of rubber acquired, discontinuance or adjustment of certain projects (including the cryptostegia project), disposal of excess stocks in the United States, personnel, aviation activities, and the need for natural rubber. While the report is somewhat lengthy, it nevertheless represents only a relatively brief review of the

more salient features of the operations of the government agency since its inception. [From *The Rubber Age* of New York.]

**1945 YEAR BOOK OF THE CHICAGO RUBBER GROUP.** Published by the Group (W. F. Bernstein, Secretary-Treasurer, 1 No. LaSalle St., Chicago 2, Ill.). 8¼ x 11 in. 48 pp.—This first year book issued by the Chicago Rubber Group is dedicated to "the advancement of rubber technology". For a first attempt it is a laudable issue, and contains interesting data. In addition to listing the 1944 officers of the group, as well as past chairmen, committees, and complete lists (with company connections and telephone numbers) of both Chicago and out-of-town members, the book contains data on rubber testing instruments manufactured in the Chicago area, tables and charts on the properties of various synthetic rubbers, a classification of carbon blacks by types, brand names, manufacturers and uses, and other information. The complete by-laws of the group are reproduced in the year book and some photographs taken at the group's last outing are shown. Commercial advertising is sprinkled liberally throughout the book. [From *The Rubber Age* of New York.]

**CARE AND USE OF SYNTHETIC RUBBER TIRES.** (Maintenance Bulletin No. 41). Highway Transport Dept., Office of Defense Transportation, Washington, D. C. 8 x 10½ in. 18 pp.—This bulletin discusses use and maintenance practices which have the greatest effect on tire-casing life. Also included is current information regarding the peculiarities of the synthetic-rubber compounds now used in tire and tube manufacture. From this information about the nature of synthetic materials, truck or bus owners may gain a better understanding of the limitations of such materials and be able to do a better job in saving the tire casings which are available. Items which influence only tread wear are not discussed in the bulletin. [From *The Rubber Age* of New York.]

**SURFACE CHEMISTRY.** Publication of the American Association for the Advancement of Science, No. 21. Edited by Forest Ray Moulton. American Association for the Advancement of Science, Smithsonian Institution Building, Washington, D. C., 1943. 160 pp. 19 x 26.5 cm. Price to members, \$2.75; to others, \$3.25.—The American Association for the Advancement of Science has made a definite contribution by publishing this volume. It is based on a symposium in commemoration of the twenty-fifth anniversary of W. D. Harkins' first publication in this field. The subject is of profound theoretical interest and it is also of prime practical importance both for many technological problems and for the understanding of fundamental physiological processes. It is of more general interest than might be suggested merely by looking at the table of contents. Fifteen of the leading authorities in this country participated in the contributions here made available. One deals with interactions of biologically significant substances such as carcinogenic hydrocarbons with surface films, illustrating this important approach to biology. Then Langmuir and Schaefer discuss the effect of surface films on evaporation. The pièce de résistance is Harkins' résumé of his life work in this field, together with the references to 111 papers by Harkins and his collaborators. The reviewer takes the opportunity of referring to another comprehensive discussion by Harkins in Jerome Alexander's "Colloid Chemistry", Vol. V, Reinhold Publishing Corporation, New York, 1944, pp. 12 to 102. G. E. Boyd discusses the results of the Chicago school dealing with the difficult subject of the sur-



faces of solids. Other contributions deal with orientation, polarity, rate processes, and intermolecular attractions in and between surfaces. These are also related to problems of friction and lubrication, as well as to the nature of cohesion and catalysis. Two other papers are concerned with the elasticity of rubberlike materials, and with diffusion and viscosity in protein solutions. Nowhere else is all this important material so conveniently brought together. [From the *Journal of the American Chemical Society*.]

**TIRES AT WAR.** Rubber Manufacturers Association, 444 Madison Ave., New York, N. Y. 11 x 8½ in. 8 pp.—The job done by the American tire manufacturing industry in meeting the near-impossible to maintain both military and essential civilian transportation is outlined in this statistical booklet. Figures on the production of airplane tires and truck and bus tires for the years of 1939 to 1944 are given, as well as statistics on passenger car tire production, camelback, crude and synthetic rubber, and cotton and rayon. All figures are given textually and by clearly drawn graphs. [From *The Rubber Age* of New York.]

**VARNISH CONSTITUENTS.** By H. W. Chatfield. Science Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y., 1944. 496 pages. 14 x 22 cm. Price, \$7.00.—This book contains a detailed description of the many diverse materials which are available for use in the manufacture of oleoresinous varnishes. There is some discussion of the methods of manufacture of some of these raw materials, especially where variations in the manufacture results in different grades or varieties which the varnish maker needs to distinguish. The main emphasis is on the properties of the materials which influence or control their suitability for varnish making. The author evidently attempts to give definite numerical values of measurable properties wherever feasible. A substantial fraction of the book is devoted to tables in which the numerical values of significant properties are systematically tabulated for easy reference and comparison. There are such tables for Varnish Oils; Acids; Monoglycerides; Synthetic Resins (47 pages); Solvents and Diluents (22 pages); Plasticizers (16 pages); Driers, Salts and Soaps; Asphaltums and Pitches, Waxes; besides numerous small tables of varied sorts. Numerous references to the technical and patent literature are given. The text contains much descriptive matter and comments on performance and usefulness of the materials with a discussion of the possibility of substitution of one material by another and the influence of such replacements on the properties of the finished varnish. Since these comments are written by an experienced English expert, they should be of value to American formulators in these days when shortages of materials and priorities may make substitutions necessary. Statistical data as to production and international commerce in these materials are omitted, and what little comment there is on such questions is apt to be weak. Thus under the heading Soya Bean Oil he says, "The oil is obtained from the beans of *Glycine* or *Soya hispida*, indigenous to China, Japan and Manchuria. Some oil is produced in the United States of America, Russia and Europe, and a little from experimental sources in Great Britain". The author apparently is not aware that the production of soya bean oil has been gaining rapidly in the United States. In 1943 the production in the United States was 1226 million pounds, which was almost as much as the cottonseed produced (1312 million pounds) and substantially ahead of the linseed oil (917 million pounds). [From the *Journal of the American Chemical Society*.]

**COMMERCIAL WAXES: NATURAL AND SYNTHETIC.** Edited by H. Bennett. Published by the Chemical Publishing Co., Inc., 26 Court St., Brooklyn, N. Y. 5½ x 8½ in. 583 pp. \$11.00.—This book is both a symposium and compilation of data on natural and synthetic commercial waxes, including properties, uses, methods of handling and formulas for making commercial wax compositions. All classes of waxes, such as mineral, animal, vegetable, insect, synthetic and compounded waxes, are discussed in detail, with data on melting point, form and fracture, purity, hardness, flexibility, moldability, adhesiveness, solubility, and other properties. Sources and uses of each type of wax are outlined. One section is devoted to the handling and compounding of the various waxes. The use of wax in rubber compositions is briefly discussed and a few formulas of rubber wax compositions are included. The book also includes a glossary of terms and a subject index. [From *The Rubber Age* of New York.]

**FORMALDEHYDE.** J. Frederic Walker. American Chemical Society Monograph Series. Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1944. Cloth, 9¼ by 6 inches, 397 pages. Price \$5.50.—No single book dealing with formaldehyde has heretofore been available in the English language. This one, by J. Frederic Walker of the Chemical Research Division, Electrochemicals Department, E. I. du Pont de Nemours & Co., Inc., fulfills the need of such a book created by the growing importance of formaldehyde as a commercial chemical. It covers production methods; the physical and thermodynamic properties of the simple monomer, formaldehyde solutions, and polymers; chemical properties and reactions with various types of inorganic and organic chemicals; analysis; and industrial applications. A chapter is also given to hexamethylenetetramine, which is industrially important as a special form of formaldehyde. The use of formaldehyde in the handling of rubber latex, the production of crude rubber, the preparation of rubber derivatives, and the synthesis of rubber accelerators and antioxidants is briefly treated. Its potential applications as a raw material in the synthetic rubber industry for the synthesis of dienes is pointed out, and the reaction of sulfur and alkali-metal sulfides with formaldehyde to obtain rubberlike materials is described. The value of formaldehyde in the production of solvents and plasticizers are also discussed. For security reasons new wartime uses of formaldehyde are not disclosed. [From the *India Rubber World*.]

**COMMERCIAL METHODS OF ANALYSIS.** Foster Dee Snell and Frank M. Biffen. International Chemical Series. McGraw-Hill Book Co., Inc., 330 W. 42nd St., New York 18, N. Y. 1944. Cloth, 8½ by 5¼ inches, 760 pages. Index. Price \$6.—Clear, concise, and dependable methods for the practical analysis of numerous commercial products currently used appear in this volume. Methods given are those which a commercial laboratory will find practical for considerations of economy and time without the sacrifice of the reliability of results. They are, for the most part, standard methods, such as those approved by the American Society for Testing Materials and other chemical societies. Standard methods are not always described completely, and some have been simplified; but explanations of steps, the reasons for which are not immediately clear, have been added. Methods, other than standard and shorter, are sometimes given. An important feature of the book is its presentation of a method of approach to the analysis of complex commercial products, many of which provide inexperienced chemists with difficulties.



Two chapters are devoted to rubber. Qualitative and quantitative analyses, largely according to A.S.T.M. methods, are outlined. There are tests for determination of rubber hydrocarbon, rubber as compounded, artificial aging, determination of copper and manganese, analysis of latex, tests for gutta-percha and balata, and identification of various types of accelerators. No tests are given for the synthetic rubbers, but there is a brief discussion of their similarities with and differences from natural rubber. Other chapters contain analytical procedures for sulfur and its compounds, solvents and thinners, synthetic resins, pigments, extenders, mineral fillers, oil and wax emulsions, and other chemicals. [From the *India Rubber World*.]

INDUSTRIAL ALCOHOL. Report No. 2, War Changes in Industry Series. United States Tariff Commission, Washington, D. C. 52 pages.—Because the postwar status of the alcohol industry may be materially affected by the size of the synthetic rubber industry and the methods by which synthetic rubber is made, the postwar future of the synthetic rubber program is of fundamental importance to producers of industrial alcohol. This report discusses the various factors, including synthetic rubber, which will likely govern alcohol production and consumption after the war. [From the *India Rubber World*.]

CHEMICAL ENGINEERING CATALOG 1944-45. Twenty-ninth Annual Edition. Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. 1580 pages.—This catalog is primarily a source of information to manufacturers and their sales agents. The products of more than 600 firms are listed under two headings—equipment and supplies, and chemicals and materials. There are also a trade name index and a section with brief descriptions of selected technical publications. [From the *India Rubber World*.]

SEEING THE INVISIBLE. The Story of the Electron Microscope. Gessner G. Hawley. Alfred A. Knopf, Inc., 501 Madison Ave., New York, N. Y. 1945. Cloth, 7½ by 5 inches, 204 pages. Price \$2.50.—This simplified and personalized account of the development and use of the electron microscope was admittedly written to interest laymen. Only the most essential scientific principles are introduced, and these are thoroughly explained in nontechnical language. The details of the construction and operation of the instrument are briefly given, but the principal concentration is on the electron microscope's applications to current and future problems of practical interest. Some attention is given to its use in carbon black investigation and research on synthetic rubber and natural and synthetic latex. There are more than 70 illustrations and a number of simple diagrams which help to make clear the scientific principles involved. [From the *India Rubber World*.]

THE SOCIETY OF THE PLASTICS INDUSTRY 1944-1945 DIRECTORY. Society of the Plastics Industry, Inc., 295 Madison Ave., New York 17, N. Y. 1944. 248 pages. Price \$2.50 to non-members.—This comprehensive directory lists more than 400 United States, Canadian, and foreign companies engaged in molding, extruding, fabricating, and laminating plastics and in manufacturing plastics material and machinery. Officers, addresses, and products are given. There is also a lengthy "Who's Who in Plastics" and classified product, material, and machinery indexes. [From the *India Rubber World*.]

A TREATISE ON THE MATHEMATICAL THEORY OF ELASTICITY. By A. E. H. Love. Published by Dover Publications, 1780 Broadway, New York 19,

N. Y. Cloth, 6 by 9 inches, 662 pages. Price \$3.95.—This is the 4th, revised edition. The work has been for years the standard treatise on elasticity. It combines a wealth of practical applications with a thorough, rigorous discussion of fundamentals, and is an indispensable reference tool for the mathematician, physicist, and engineer whose work involves problems in elasticity. Starting with an historical survey, the author discusses the analysis of stress and strain, elasticity of solid bodies, equilibrium of isotropic elastic solids, elasticity of crystals, vibration of spheres and cylinders, propagation of waves in elastic solid media, torsion, the theory of plates, etc. The general theory of stress and strain, problems of equilibrium, treatment of two-dimensional elastic systems, and the analysis of crystal elasticity will be of interest not only to the pure and applied physicist, but also to the mathematician, who will find a rigorous, elegant treatment of Volterra's theory of dislocations, two-dimensional elastic systems, the theory of the integration of equations of equilibrium of an isotropic elastic solid body, and other subjects.

RUSSIAN-ENGLISH AND ENGLISH-RUSSIAN DICTIONARY. Edited by M. A. O'Brien. Published by Dover Publications, 1780 Broadway, New York 19, N. Y. Cloth, 4½ by 6½ inches, 720 pages. Price \$1.98.—With the flood of scientific and technical literature expected from Russia, more and more scientists and technologists face the problem of consulting original papers in Russian. This dictionary contains 35,000 terms in the Russian-English section and 35,000 terms in the English-Russian section. Different shades of meaning of Russian words and phrases are given so that the user can rely upon accuracy of translation and understanding of the connotations of each word and the particular meaning in each field of knowledge. As an aid to those with limited familiarity with Russian, parts of speech are indicated; sound changes, gender, and irregularities of declension of nouns are given; verbs are listed in perfective and imperfective aspects; conjugation of present tenses is indicated; the conjugation of irregular verbs is tabulated; adjectives with irregular comparisons are given in both positive and comparative forms; and cases governed by prepositions are given. Conversion tables of Russian weights and measures are included. The dictionary is recommended in the Standard Catalog for Public Libraries, and is endorsed and used by the Slavic Departments of Harvard University, Yale University, Cornell University, the American-Russian Institute, etc.

## SPECIFIC INFLUENCES IN THE POLYMERIZATION OF DIENES

### CHEMICAL FACTORS INFLUENCING THE HOMOGENEITY OF SYNTHETIC RUBBERS DURING PRODUCTION \*

WILLIAM S. PENN

At the present time, when so much synthetic rubber is being produced, the question of the polymerization of dienes is most important. Many thousands of tons of GR-S and related rubbers are being made by this means, and yet the process is only very imperfectly understood. Polymerization is still an uncontrolled reaction, although much work has been done in an attempt to overcome the deficiencies.

The troubles are caused by the fact that the dienes do not polymerize in a regular way, because of the formation of branch chains and cross-linkages, which are a direct result of these branch chains. These irregularities must be controlled before satisfactory products can be obtained, and the present paper is written to correlate isolated evidence and present fresh material so that the processes involved during polymerization may be more perfectly understood and possibly controlled.

It is natural in the first instance to examine natural rubber to see if any indication of the lines to follow can be obtained. Unfortunately, however, even natural rubber is not perfect, and from various sources of evidence<sup>1</sup> it has been shown that branching does occur in the isoprene chains. This branching is, however, different from that in synthetics, and is quite regular. As will be seen shortly, it is difficult on chemical or physico-chemical grounds to see why this should be so, as the only directive group in the isoprene unit is the methyl side-group. It seems logical to conclude that natural rubber is not formed by a polymerization process, but that carbon and hydrogen atoms combine in such a way that they form directly a natural rubber-molecule.

In the first instance an investigation into polymerization processes means that many factors have to be controlled, apart from the chemicals themselves. Temperature, pressure, light and the presence of catalysts, inhibitors (either of which may be the reaction vessels themselves) and solvents, all affect the polymerization to a great degree. To quote an example, the case of dimethylbutadiene and isoprene<sup>2</sup> may be mentioned. At high temperatures the former polymerizes much more slowly than the latter, but the conditions are reversed at room temperatures. Also, it should be remembered that the medium of polymerization is most important, and products formed during gaseous reactions, in solvents, in emulsions and in the pure liquid compound itself are quite different. The reactions discussed in the following pages usually took place in emulsion form.

In the investigations which follow, two main criterions of effectiveness of polymerization are usually taken into account. These are the speed of reac-

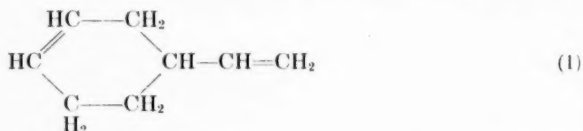
\* Reprinted from the *India-Rubber Journal*, Vol. 107, No. 13, pages 345-348, September 23, 1944, and No. 14, pages 373-376, September 30, 1944.

tion, the degree of polymerization, and whether the latter allows the development of rubbery properties. Sometimes one substance polymerizes much more rapidly than another, but more often than not a dimer is formed, which is of little use as an elastomer.

#### UNSUBSTITUTED DIENES

The great importance of side groups in controlling the polymerization of dienes will be the main theme of this paper. First, however, the simpler case of butadiene, which has no asymmetric side groups, will be described. This will be of use in the more complex instances. I purposely mention the word asymmetric above because, if the hydrogen atoms in butadiene are regarded as being side groups, they are symmetrical with respect to the carbon atoms and double bonds, and therefore exert little specific influence on the direction of reaction of the butadiene.

It has been shown<sup>3</sup> by x-ray analysis that the carbon atoms of the butadiene unit lie in the same plane, and this point is of some significance in the polymerization of butadiene. Under some conditions, *e.g.*, polymerization by heat<sup>4</sup>, a dimer is formed at the same time that the polymer is produced. The ratio of dimer to polymer is constant at constant temperature, although the amount of dimer increases with temperature. The phenomenon of the formation of a dimer is common among dienes, and therefore the temperature in these reactions should not be allowed to rise too high, so as to avoid this undesirable side reaction. The dimer is ethylene cyclohexene or 1-vinyl-3-cyclohexene:

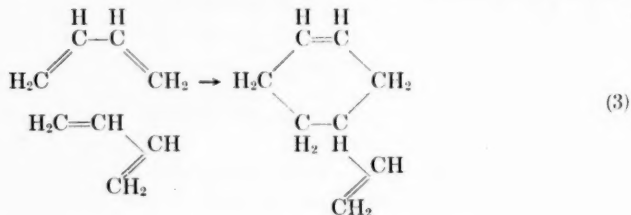


From an examination of the formula of butadiene, it is easy to see how this cyclic compound can be formed. In space, butadiene is shaped somewhat as in (2):



This configuration is not static, of course.

Now on strain considerations, if a five or six membered ring cannot be formed, polymerization usually takes place; therefore if two butadiene molecules approach in the way shown in (3) below, a dimer is practically certain to be formed.



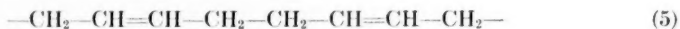
It is extremely improbable that an eight-membered ring forms.

To illustrate other points mentioned above, such as change of phase if polymerization takes place in the gaseous phase (as distinct from the liquid phase), compound (4) is formed<sup>5</sup>.

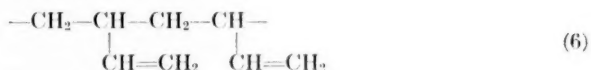


Now in spite of the fact that butadiene is symmetrical, it can polymerize in three main ways.

(1) By regular 1,4 addition, as shown in (5):



(2) By regular 1,2 addition, as shown in (6):



(3) By chain branching, with the double bonds in one chain combining with those in others.

There may also be combinations of any of these particular means.

Ozonolysis of a butadiene polymer<sup>6</sup> made in an emulsion yields succinic acid, 1,2,4-butanetricarboxylic acid and resinous acids. This shows that butadiene, polymerized in emulsion form, polymerizes by all these methods. There are no quantitative figures available in this connection, but it can be estimated that in the first instance (1) and (2) contribute 50 per cent each to the process. A few per cent of the branched chains in (2) are then utilized for the formation of cross-linkages, as in (3). From other considerations it appears that at least 50 per cent of the polymer is composed of alternate 1,4 and 1,2 constructional units. It therefore seems that the vinyl groups in butadiene are quite directive, and exert a strong influence on the course of the reaction.

This point is best illustrated by reference to the polymerization of butadienes by alkali metals. The two examples are actually not strictly comparable, as the one just described takes place in emulsion form, and the one about to be described takes place in liquid phase. The results, however, although not quantitatively comparable, do form the basis for discussion.

The action of sodium on butadiene is too rapid. It can be slowed up conveniently for purposes of observation by the substitution of lithium<sup>7</sup> for sodium, the replacement of butadiene by dimethylbutadiene, and by diluting with ether. The methyl groups probably affect only the speed of the reaction and not the course. They are disposed symmetrically with respect to the butadiene molecule, and any specific influences are exerted equally in opposite directions.

The compound first formed is (7) below:



and this then reacts with more dimethylbutadiene to form (8):



A final series of compounds are then formed represented by (9):

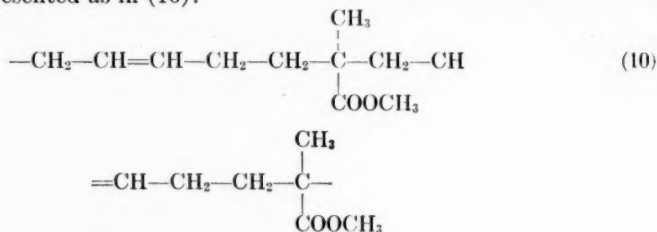


Analysis indicates that in both these lithium polymers and other alkali polymers the products formed are quite regular, the structure being a regular alternation of 1,4 and 1,2 combination. This illustrates once more the specific directive influence of the vinyl group.

### COPOLYMERIZATION

The object of this paper is to find some means of directing the polymerization of dienes to make synthetic rubbers so that a regular product is obtained. After preliminary observations on the polymerization of butadiene, the next logical step is that of copolymerizing with other substances. These exert a certain directive influence on the course of the reaction, and this is the way adopted to produce the general purpose synthetic GR-S. It might seem out of place to introduce this in the middle of a paper, and it might possibly be thought that, as it is apparently the climax, it should come at the end. I cannot agree with this view, however, as the present GR-S is certainly not the best, most consistent rubber which can be produced, and the climax of synthetic rubber production is yet to come. I do not maintain, of course, that GR-S has been stated to be the best possible synthetic, but merely make the statement to justify my discussion of copolymerization at this point.

An enormous amount of work has been, and is still being done, on copolymerization. The results are not encouraging, as no copolymer has been found which is regular in its molecular construction. Many of the copolymerization processes which have been studied have yielded very irregular polymers. In fact, results have often been more involved than those involving the polymerization of butadiene alone. The copolymerization of butadiene with methyl methacrylate may be quoted as an example. The copolymer was made by polymerizing equimolecular quantities of the two compounds in emulsion form. Ozonolysis shows that about half the copolymer is regular, composed of alternate units of butadiene and methyl methacrylate. This is shown by the formation of 2-methyl-1,2,4-tricarboxylic acid, which also shows that butadiene reacts mainly in the 1,4-position. The remainder of the copolymer is very varied, showing that the methyl methacrylate is not very directive. The copolymer is represented as in (10):



Advancing a stage further we may now take the case of the copolymerization of butadiene and acrylonitrile<sup>8</sup>. The copolymer in the experiment was produced from a 50/50 mixture of the two components. Ozonolysis again shows that one-half of the polymer consists of alternate units of butadiene and acrylonitrile and one-third of molecules in which butadiene corresponds to two or three molecules of acrylonitrile. It is seen that the directive influence of the acrylonitrile is more powerful than that of the methyl methacrylate. It seems logical to suppose that this is in some way due to the nitrile group, because this is the main difference between acrylonitrile and methyl meth-



acrylate. Proceeding further, therefore, in this direction, equimolecular parts of butadiene and methacrylonitrile have been copolymerized<sup>9</sup>, and the results of this are most encouraging. Most of the polymer consists of alternating links of the two materials, with the butadiene in the 1,4-configuration. A definite step has been made, therefore, towards establishing a more regular rubber. It might be as well to mention at this point that none of these polymers or copolymers give x-ray diagrams which show them not to be orderly like natural rubber molecules. This is quite understandable, however, since even if branching only occurs to the extent of a few per cent, any cross-linkages which could be formed would probably be enough to destroy any possible chance of orientation taking place.

There are many more copolymers which could be cited, of course, but they would be superfluous. It is now established that the nitrile group has some specific influence in directing the course of polymerization, and it does show that these directive influences are most important.

We now arrive at the final stage of this section, the copolymerization of butadiene with styrene. Either rightly or wrongly, and I will venture an opinion on this later, at least from the chemical point of view, it was decided that, for the general purpose synthetic, butadiene should be copolymerized with styrene. Some information is again given by Alekseeva<sup>10</sup> in this connection. He made an equimolecular mixture of the two molecules and polymerized them. The results may be summarized as follows. About 31 per cent of the styrene forms polymers with butadiene, in which the components alternate regularly with the butadiene in the 1,4-position. About 40 per cent of the styrene forms polymers in which two molecules of styrene are separated by one or more molecules of butadiene. The remainder (29 per cent) is mainly a branching operation in which the butadiene is linked in both the 1,2- and 1,4-positions. Taking overall values, it is estimated that 23.3 per cent of the polymer contains butadiene in the 1,2-configuration and the remainder in the 1,4. It will be seen that, although there is some regularity in this copolymer, it is not so great as that in the butadiene and methacrylonitrile copolymer.

One point of significance in these results is that 40 per cent of the copolymer consists of an arrangement where two molecules of styrene are together. When this fact is applied to GR-S production, it means that the styrene is not going to be spread very evenly over the chain of the molecules. This is possibly one of the reasons why GR-S is so variable.

Even the arrangement which is attained in the 50/50 copolymer is lost when the copolymer becomes 75/25 butadiene-styrene. If the styrene were spread evenly over the molecules, there would be the same number of polymerizable double bonds per unit length (ignoring cross-linking and branching for a moment), and an even GR-S would be realized. As it is, the material is most heterogeneous, and I suggest it is because the styrene is such a weak directive influence. This is also the reason for the excessive amount of branching which takes place, as will be explained later in detail.

It is, perhaps, significant that in the development of GR-S latices, the 50/50 copolymer has been decided to be the best. For special purposes this will be used, and it has been shown to give films much superior to those from ordinary GR-S latex. The superior regularity of the 50/50 copolymer is the reason for this, but I would point out that the advantage of the 50/50 copolymer over the 75/25 is merely one of quantity, not quality.

Apparently, therefore, it is not possible, at least on the evidence yet available, to produce a satisfactory synthetic rubber by the process of copolymeri-

zation. From the facts it would seem that some group might have a sufficiently strong directive influence to effect the desired result, but up to the present this has not been found, and so we shall have to look further afield.

#### SUBSTITUTED DIENES

Many dienes, in fact isoprene itself, which is the basic unit of natural rubber, are substituted in some part of the molecule. This affects to a very great degree the polymerizability of the dienes and the resultant synthetic rubbers. It is safe to say that it is the greatest factor in controlling the production of synthetic rubbers, yet up to the present little advantage has been taken of it. Once again the logical step is to start with the simplest substituent (as far as organic radicals are concerned) and this is, of course, the methyl group. 2-methylbutadiene, more commonly known as isoprene, was one of the first dienes to be examined in an attempt to produce a synthetic rubber.

It was assumed, not without some justification, that as the basic unit of natural rubber is isoprene, this material should produce a good synthetic rubber. This proved to be fallacious, although why is still a puzzle. As mentioned at the beginning, it has been shown that natural rubber has branching in its molecules, but this is very regular. This suggests that the methyl group has a powerful directive action, but when attempts have been made to take advantage of this property they have failed badly.

Isoprene polymerizes rather sluggishly to give a fair rubber. It may conveniently be taken as the standard, and will be treated as such in the arguments which follow.

From isoprene the next logical materials to try are butadienes substituted in the 2-position with members of the homologous series, beginning with methyl. The outstanding one which has been tried is the heptyl group<sup>11</sup>.

2-heptylbutadiene polymerizes about nine times as fast as isoprene, but the rubber produced is a soft sticky compound, and certainly not so valuable as rubber from isoprene.

The next diene to examine is one with more than one methyl group. Dimethylbutadiene is a good example<sup>12</sup>. This polymerizes more rapidly than isoprene to give a fair rubber of low extensibility. When the methyl groups are attached to the terminal positions, the polymerizability drops enormously. From an examination of this and many similar compounds, it has been shown that, for the production of a satisfactory rubber at a reasonable speed, the end groups must be unsubstituted. There is one important exception to this statement, however, 4-cyano-1,3-butadiene<sup>13</sup> (11).



In spite of the fact that substitution is in the terminal position, this substance polymerizes about twenty times as fast as isoprene. This may be because of the extra conjugation due to the nitrile group. It goes once more to show the importance of the nitrile group in these matters.

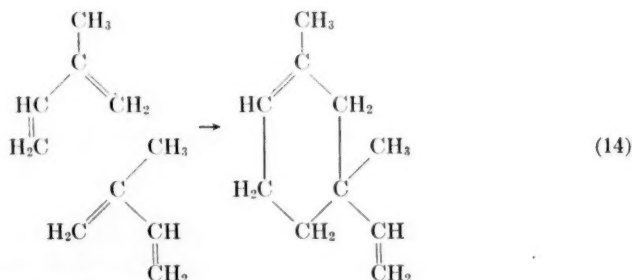
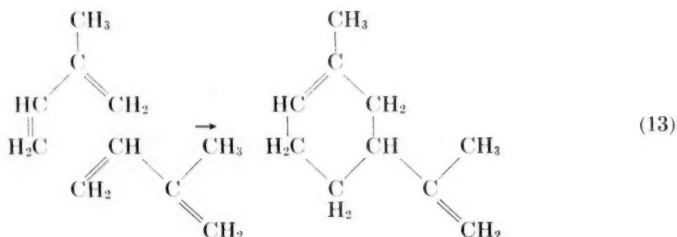
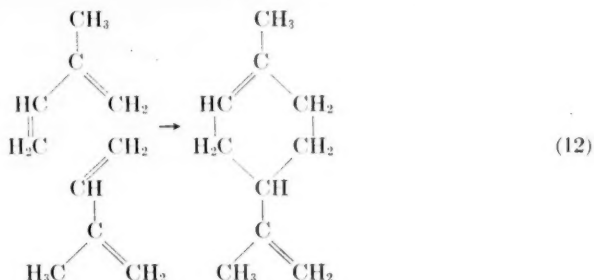
Up to the present specific influences on the structure of the rubbers have not been mentioned. These various molecular substituents have been described as affecting the speed of reaction and possibly the physical properties of the rubber formed, but not as affecting the structure of the rubber, with which we are primarily interested. Suffice to complete the discussion on these substituents, therefore, by saying that many have been tried, and they all give



different speeds of polymerization. The general conclusions have already been mentioned.

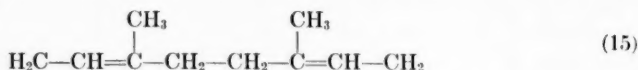
It is best to start the discussion of the structure from this point of view by examining the polymerization of dimethylbutadiene under certain conditions. When heated at certain temperatures, the product is mainly a dimer, 4,6-dimethyl-6,8-menthadiene, and this does not polymerize further<sup>14</sup>. This phenomenon is not greatly noticeable with butadiene, and so we must put it down to the presence of the two methyl groups, which direct, under certain conditions, the reaction in this particular direction. This applies also to polymerization by the action of lithium. The reaction is not by any means peculiar to 2,3-dimethylbutadiene. All dimethylbutadienes, phenylbutadienes and many others, including isoprene, do this.

Isoprene is the most interesting from our point of view, for it dimerizes very easily under certain conditions<sup>15</sup>, mainly at high temperatures. Wagner-Jauregg summarized the dimerization as follows<sup>16</sup> (12, 13, 14).



All that can be concluded from this is that the directive influence of the organic groups so far examined is very weak, and that the particular spacial arrangement of the dienes concerned contributes most towards the particular

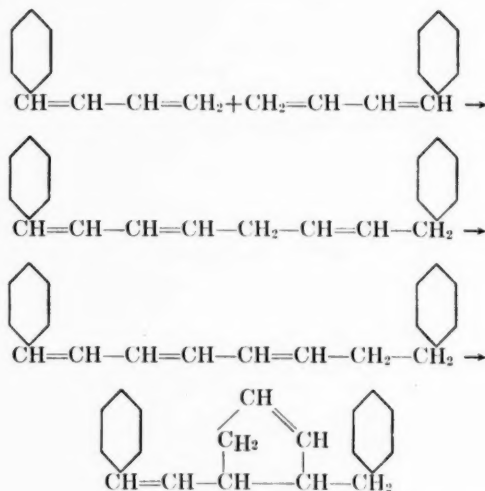
polymerization. This is illustrated further by another way in which isoprene can be polymerized. Purified isoprene, mixed with potassium and alcohol so that hydrogen is evolved, gives a good yield of a bright yellow oil. This proved to be a mixture of 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadiene (3,6 illustrated below (15)).



No traces of cyclic dimers are formed in this instance, and it is indicated that the compounds are long chains produced by the interlocking of 1,4-carbon atoms<sup>17</sup>.

Finally in connection with the organic radicals, the case of 2-phenylbutadiene may be described<sup>11</sup>. This polymerizes much more rapidly than isoprene, yet all the compound produced is practically invariably a cyclic dimer. This is by all methods of polymerization. It shows that the phenyl group is particularly directive in the polymerization process, but not as we require it, for the production of long-chain molecules.

In view of the fact that the phenyl group is attached to the GR-S molecule, this point is worthy of further investigation. Some cyclization may take place in GR-S, due to the directive influence of the phenyl group, and this may be one of the reasons for the low viscosity of GR-S (the other is, of course, due to branching and cross-linking). The situation is best summed up by Bergmann<sup>18</sup>, who considers that cyclization and dimerization of 1-phenylbutadiene take place as follows (16):



This is one more reason why styrene is not a suitable molecule to copolymerize with butadiene.

As I have stressed, we have up to the present considered organic groups substituents. There is another class, however, which appears to offer more hope of a satisfactory rubber, and this will now be examined. This is with inorganic substituents, notably the halogens. The polymerization of chloroprene to produce Neoprene is well known, and it is this substance which will form the basis of the following discussion.

Neoprene was the first synthetic rubber which, on stretching and examination with x-rays, gave a crystalline diagram. All the other synthetic rubbers up to then produced from dienes (including GR-S), gave an amorphous diagram on stretching and examining with x-rays. This seemed to suggest that polychloroprene was more orientated than the other synthetics, and some means had been found of directing the polymerization along regular lines.

Chloroprene polymerizes much more rapidly than isoprene, and the rubber so produced is much more satisfactory. This seems to be due entirely to the directing influences of the chlorine atom. Troubles, however, are still experienced with Neoprene, which suggests that it is not by any means free from cross-linkages. It is definitely more regular than other synthetics, however, which shows that we are now more on the right lines. Chloroprene polymerizes generally in quite a regular manner in the 1,4- and 4,1-positions<sup>19</sup>, but as far as can be seen rarely in the 1,2-position. I believe that there are few cross-linkages caused by mutual saturation of double bonds in different chains, and any that are produced come from the elimination of the relatively mobile chlorine atoms.

Once more, taking the process a stage further, the polymerization of 2,3-dichloro-1,3-butadiene was examined. This polymerizes even more quickly than chloroprene, but the rubber so produced is harder and tougher than Neoprene. x-Ray examination showed that it is not so regular as Neoprene, which is to be expected, in view of the fact that the directive influence of the chlorine atoms is now about equal in both directions. In any case it is surprising that this symmetrical substituted diene should polymerize at all, for in the parallel case of sym-dichloroethylene, no polymerization takes place at all. Perhaps, however, the difference is due to the presence of the  $:\text{CH}_2$  group.

Furthermore, chlorine atoms and other substituents<sup>20</sup> depress the polymerizability of chloroprene, and therefore other means will have to be found to improve the superior properties developed, due to the use of chloroprene.

The logical step is, of course, bromobutadiene, or bromoprene<sup>21</sup>. This compound polymerizes more readily than chloroprene to yield a reasonably satisfactory rubber. However, this is rather sluggish, and in some instances has a fair amount of permanent set, although it is resilient and tough. The toughness and sluggishness are probably due to the high molecular weight of the bromine. However, what is important at this point, the polybromoprene gives an even sharper x-ray diagram than Neoprene, showing that the bromine atom has an even more directive influence than the chlorine atom.

Going still further, 2-iodobutadiene polymerizes even more rapidly than the other halogenated molecules, but yields a substance which is rubbery only under certain conditions. x-Ray examination in the rubbery phase shows this molecule to be well orientated, illustrating that a molecule with greater directive powers has been found.

We cannot at this point proceed any further on evidence yet available.

There are certain objections, both economic and chemical, to the use of either bromine or iodine as directive influences. We may, therefore, summarize the situation, draw conclusions, and make suggestions for further work.

We have seen primarily that organic radicals are of little use as directing influences. More often than not dimerization or possibly cyclization takes place, at least as a side reaction. Copolymerization offers some possibilities especially with groups containing C:N. However, the most promising method seems to be by the use of a halogen-substituted butadiene. I should imagine that the ideal rubber would be synthesized by a copolymer of a halogenated

butadiene and a substance containing one double bond and a C≡N grouping in some position. It is interesting to note in this connection that copolymers with chloroprene are now being made which may follow along the lines suggested. Obviously a copolymer with iodoprene should provide a highly orientated rubber, especially if there is not too much iodoprene present to create mobile halogen.

Before closing, one further reference should be made to a paper already discussed<sup>3</sup>. This is the one by Bunn on the x-ray examination of gutta-percha, natural rubber and polychloroprene. It has been ascertained that, although polychloroprene is not so regular in its molecular configuration as the other two compounds, its unit cell is the same as that of gutta-percha, showing that Neoprene is getting on towards the rubber which we require. The day should, therefore, not be far ahead when we shall be able to produce a special-purpose synthetic rubber which is the equal of the natural product.

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## THE KINETICS OF POLYMERIZATION REACTIONS \*

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In dealing with the kinetics of polymerization reactions formally similar to the classical chain reactions, some considerable extension to the theory has been necessary to cope with the additional complexity of the mechanism of the formation of macromolecules. The most important extension is that it is necessary to discriminate carefully between those reactions in which the average life-time of the active polymer is less than the half life of the monomer and those in which the life-time is comparable to or greater than the monomer half life. There is now considerable evidence that both types of reaction occur even with the same monomer, depending on the nature of the initiation process. The other important fact is that examination of the "dead" polymers left after the reaction is brought to a stop not only enables an average value of the kinetic chain length to be obtained, but also makes possible the determination of the distribution of molecular weight about the mean value. If this latter source of information may be accurately acquired, and this cannot be said yet of even the best fractionation, it provides yet another check on the mechanism of synthesis, as will be shown later on in this paper.

The simplest way to tackle the kinetic analysis of polymerization is to assume that all active polymers are identical in reactivity, that is, the velocity coefficients of the various reactions that the active polymer may undergo do not vary with molecular size. Making this assumption, it is an easy matter to work out all the possible types of reaction which might be encountered according to the classical stationary state method<sup>1</sup>. If, however, the analysis is to be done in detail, it is necessary to take into consideration that the velocity coefficients vary with molecular size, even though there is no evidence in any polymeric reaction just what sort of variation is to be expected. In the early development of polymerization kinetics, it was suggested that the simplest way out of the difficulty was as follows. In all reactions in which the life-time of the active polymer is small, it is found on analysis that the rate expression contains a factor giving the ratio of the propagation to the termination velocity coefficients. Since any variation in the velocity coefficient of the growing polymer is, so to speak, inherent in the polymer itself, such a reaction will be reflected in any reaction-propagation or termination which the polymer may undergo. Thus, if we suppose that the ratio of the coefficient is independent of molecular size, at least a first approximation will be obtained. Conversely, this implies that any kinetic investigation will never reveal any variation in the magnitude of their coefficients for the simple reason that in the rate equation there are three unknown coefficients, and only two pieces of information are at present obtainable from experimental data, namely, the overall rate of reaction, and one of three equivalent pieces of information, namely, kinetic

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chain-length, rate of starting of chains, rate of cessation of growth. This simple assumption about the ratio of coefficients has been used in a number of kinetic analyses. But it can also be used to calculate molecular-weight distributions arising from the different kinds of reaction now well recognized in polymer reactions. The purpose of this paper is to work out some of these consequences to see precisely what types of distribution curves are obtained as a result of these assumptions.

### SHORT POLYMER LIFE

In performing such analyses it is now recognized that the initiation process may be zero, first or second order with respect to the monomer concentration. It will be supposed that there is no induction period in the reaction under discussion. There is no doubt that propagation is a bimolecular reaction between active polymer and unactivated monomer. The types of termination process in absence of inhibitor are also now recognized, *viz.*: (1) monomer deactivation, *i.e.*, destruction of the activity of the polymer by a collision with monomer but naturally different from that involved in propagation, (2) spontaneous termination<sup>2</sup> in which the active polymer reverts to a stable form, and (3) mutual termination, in which two active polymers collide, the activity being destroyed either by combination or by disproportionation. The occurrence of thermal depolymerization need not be taken into account, since the reactions are almost invariably carried out at such low temperatures that thermal depolymerization is negligible and cannot therefore limit the size of the polymer. The question of transfer and of branching will be considered later.

### PHOTOCHEMICAL INITIATION WITH MONOMER TERMINATION

To indicate the principles of the method, we consider the simplest case in which the initiation is of zero order with respect to monomer concentration. This is exemplified by photo-initiation, with complete absorption of the light. The general reactions, therefore, are:



and



in which the subscripts are self-explanatory. Making the usual assumption that  $d(\text{P}_r)/dt = 0$ , and putting  $k_{t_r}/k_{p_r} = \lambda_r$ , we obtain:

$$-d(\text{M})/dt = f(\text{I}) \{ 1 + (1 + \lambda_1)^{-1} + (1 + \lambda_1)^{-1} \cdot (1 + \lambda_2)^{-1} + \dots \}$$

This equation is exact but unusable. By making the important assumption that  $\lambda_r$  is independent of  $r$ , though, of course,  $k_{p_r}$  and  $k_{t_r}$  may well not be independent of  $r$ , we obtain:

$$-d(\text{M})/dt = f(\text{I}) \sum_{r=0}^{\infty} (1 + \lambda)^{-r} = f(\text{I})(\lambda + 1)/\lambda = f(\text{I}) \cdot \lambda^{-1}$$

when  $\lambda$  is small, *i.e.*, when the chains are long. The number average chain length  $\nu_n = \lambda^{-1}$ .

To calculate the distribution of molecular sizes in the polymer, it becomes necessary to integrate the series of equations:

$$d(\text{M}_r)/dt = k_{t_r}(\text{P}_r)(\text{M}) = f(\text{I})\lambda(1 + \lambda)^{-r}$$



Further,  $\sum_{r=2}^{\infty} r(M_r) = (M)_0 - (M)$ , where  $(M)_0$  is the initial concentration of the monomer, and neglecting the concentrations of active polymers, therefore:

$$(M_r) = \lambda^2 \{ (M)_0 - (M) \} (1 + \lambda)^{1-r}$$

The weight fraction  $w_r$  of  $r$ th polymer is consequently given by:

$$w_r = r(M_r) \{ (M)_0 - (M) \}^{-1} = \lambda^2 r (1 + \lambda)^{1-r}$$

The number and weight average chain lengths  $\nu_n$  and  $\nu_w$ , respectively, may therefore be computed as follows:

$$\nu_n = \sum r(M_r) / \sum (M_r) = \lambda^{-1} \quad \text{and} \quad \nu_w = \sum r^2(M_r) / r(M_r) = 2\lambda^{-1}$$

It will be noted that for this particular mechanism the weight average is twice that of the number of average. Both these values are independent of the initial concentration of the monomer and of the extent of the reaction.

It is similarly possible to show that the curves for initiation are proportional to the first and second orders of the concentration of the monomer. This only results in the total rate becoming proportional to the first and second process of the concentration of monomer; the distribution functions remain unaltered.

*Spontaneous Termination.*—This may simply be written as  $P_r \rightarrow M_r(k_t)$ , but a reaction of such kinetic simplicity gives rise to some complications. We again consider zero order initiation as before, and for this particular case the exact rate equation reduces to:

$$\begin{aligned} -d(M)/dt &= f(I) + (M) \sum_{r=1}^{\infty} k_{p_r}(P_r) \\ &= f(I)(M)\lambda^{-1} \end{aligned}$$

for long chains.

The number average chain-length is thus  $\nu_n = (M)\lambda^{-1}$ . This now depends on the monomer concentration, and gives only an instantaneous value at the beginning of the reaction. Experimentally, however, the value is that from the start of the reaction to the time at which it is measured and is given by:

$$\nu_n = \frac{(M)_0 - (M)}{\sum_{r=2}^{\infty} r(M_r)}$$

For any mechanism:

$$d/dt \left\{ \sum_{r=2}^{\infty} (M_r) \right\} = \text{Rate of termination reaction.}$$

For a stationary state the rate of initiation is equal to the rate of termination =  $-d(M)/dt \cdot \nu_n^{-1}$ , and therefore:

$$\begin{aligned} d/d(M) \left\{ \sum_{r=2}^{\infty} (M_r) \right\} &= -\nu_n^{-1} \\ \sum_{r=2}^{\infty} (M_r) &= \int \nu_n^{-1} d(M) \end{aligned}$$

and

$$\bar{\nu}_n = \frac{(M)_0 - (M)}{\int \nu_n^{-1} d(M)}$$

But  $\nu_n = (M)\lambda^{-1}$  whence

$$\bar{\nu}_n = \frac{(M)_0 - (M)}{\lambda \ln \{(M)_0/(M)\}}$$

This tends to 0 as  $(M) \rightarrow 0$ , which cannot be correct. The error is due to the use of the approximate equation for  $-d(M)/dt$ . With the accurate expression:

$$\bar{\nu}_n = \frac{(M)_0 - (M)}{\lambda \ln \left\{ \frac{(M)_0 + \lambda}{(M) + \lambda} \right\}}$$

The rate of production of stable polymer molecules is given by:

$$+ d(M_r)/dt = k_{tr}(P_r) = \lambda f(I)(M)^{-1} \{1 + \lambda/(M)\}^{-r}$$

and therefore:

$$-d(M_r)/d(M) = \lambda^2(M)^{r-2} \{(M) + \lambda\}^{-r}$$

$$(M_r) = \lambda^2 \int_{(M)}^{(M)_0} \frac{(M)^{r-2} d(M)}{\{(M) + \lambda\}^r} = \frac{\lambda}{r-1} \left\{ \left(1 + \frac{\lambda}{(M)_0}\right)^{1-r} - \left(1 + \frac{\lambda}{(M)}\right)^{1-r} \right\}$$

The weight fraction is given by:

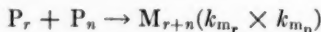
$$w_r = \frac{\lambda r}{(r-1)\{(M)_0 - (M)\}} \left\{ \left(1 + \lambda/(M)_0\right)^{1-r} - \left(1 + \lambda/(M)\right)^{1-r} \right\}$$

whence it may be shown that the value of  $\bar{\nu}_w$  is:

$$\bar{\nu}_w = \{(M)_0 + (M)\} \lambda^{-1}$$

Again, the order of the initiation reaction only makes a difference in the rate, and does not affect the distribution functions.

*Mutual Destruction.*—The mutual destruction of the active polymers leads to still greater complication in working out the distribution functions. The termination reaction is:



It is convenient to ascribe to each active polymer a separate part of the total velocity coefficient. Thus  $k_{mr}$  and  $k_{mn}$  are dimensionally different from a normal bimolecular coefficient. Account is taken of the possibility that any particular active polymer may react with any size of active polymer, and therefore the general stationary state equation is:

$$d(P_r)/dt = k_{pr-1}(P_{r-1})(M) - k_{pr}(P_r)(M) - k_{mr}(P_r)\{k_{m1}(P_1) + \dots\} = 0$$

Adopting the same procedure as before, and putting  $k_{mr}/k_{pr} = \delta$ ,  $\delta$  being further assumed to be independent of  $r$ , then for long chains:

$$-d(M)/dt = (M)\delta^{-1} \cdot f(I)^{1/2}$$

The number average chain-length depends on whether there is combination or disproportionation between the active polymers. Further,  $f(I)$  may depend



on (M). The appropriate expressions are, however, easily derivable from the above differential rate expression.

Next we consider the derivation of the distribution functions. Making use of the already mentioned assumptions:

$$k_{m_r}(P_r) = \frac{\delta \cdot f(I)(M)^{r-1}}{\{(M) + \delta f(I)^{1/2}\}^{-r}}$$

Assuming that the polymer is produced by disproportionation, then:

$$\begin{aligned} d(M_r)/dt &= k_{m_r}(P_r) \sum_{r=1}^{\infty} k_{m_r}(P_r) \\ &= \delta f(I)^{3/2} (M)^{r-1} \{(M) + \delta f(I)^{1/2}\}^{-r} \end{aligned}$$

which may be integrated to give:

$$(M_r) = \frac{\delta f(I)}{(r-1)} \left\{ \left( 1 + \frac{\delta f(I)}{(M)_0} \right)^{1-r} - \left( 1 + \frac{\delta f(I)}{(M)} \right)^{1-r} \right\}$$

and consequently:

$$w_r = \frac{r \delta f(I)}{(r-1) \{(M)_0 + (M)\}} \left\{ \left( 1 + \frac{\delta f(I)}{(M)_0} \right)^{1-r} - \left( 1 + \frac{\delta f(I)}{(M)} \right)^{1-r} \right\}$$

The weight average is likewise given by:

$$\bar{\nu}_w = \{(M)_0 + (M)\} \{\delta f(I)\}^{-1}$$

Significantly different equations are obtained when the growing polymers combine. In this circumstance:

$$\begin{aligned} d(M_r)/dt &= \frac{1}{2} \sum k_{m_x}(P_x) k_{m_{r-x}}(P_{r-x}) \\ &= \frac{r}{2} \cdot \frac{\delta^2 (f(I))^2 (M)^{r-2}}{\{(M) + \delta f(I)^{1/2}\}^r} \end{aligned}$$

On integrating this equation we obtain the rather complicated expression:

$$\begin{aligned} (M_r) &= \frac{r \delta^2 f(I)}{2(r-1)(r-2)} \left[ \left( \frac{r-1}{(M)_0} + \frac{1}{\delta f(I)^{1/2}} \right) \left( 1 + \frac{\delta f(I)^{1/2}}{(M)_0} \right)^{1-r} \right. \\ &\quad \left. - \left( \frac{r-1}{(M)} + \frac{1}{\delta f(I)^{1/2}} \right) \left( 1 + \frac{\delta f(I)^{1/2}}{(M)} \right)^{1-r} \right] \end{aligned}$$

To obtain the weight average it is necessary to evaluate  $\sum r(M_r)$ . The complete expression is extremely complicated, but simplifies on the assumption that the chain length is long, giving finally:

$$\bar{\nu}_w = \frac{3}{2} \{(M)_0 + (M)\} \{\delta f(I)^{1/2}\}^{-1}$$

#### MUTUAL DESTRUCTION WITH FIRST AND SECOND ORDER INITIATION

Owing to the occurrence of mutual destruction, the corresponding equations for the different types of initiation cannot be written down by inspection. One or two examples will be considered to indicate the general lines of approach:

*First Order Initiation.*—From the foregoing analysis:

$$-d(M)/dt = (M)^{3/2} k_i^{1/2} \delta^{-1}$$

and

$$\nu_n = (M)^{1/2} \cdot k_i^{-1/2} \delta^{-1}$$

if disproportionation occurs and  $k_i$  is the velocity coefficient for the initiation reaction. Therefore:

$$\bar{\nu}_n = \{ (M)_0^{1/2} + (M)^{1/2} \} / (2k_i^{1/2} \delta)$$

If combination occurs,  $\nu_n$  and  $\bar{\nu}_n$  are both doubled.

To obtain the remainder of the relevant equations we observe that:

$$k_{m_r}(P_r) = \delta k_i (M)^{r/2} \{ (M)^{1/2} + \delta k_i^{1/2} \}^{-r}$$

For the disproportionation reaction:

$$d(M_r)/dt = k_{m_r}(P_r) \sum_{r=1}^{\infty} k_{m_r}(P_r)$$

Unfortunately the integration of this equation leads to mathematical difficulties.

For the combination reaction, on the other hand:

$$d(M_r)/dt = r/2 \cdot \delta^2 k_i^2 (M)^r \{ (M) + \delta k_i^{1/2} (M)^{1/2} \}^{-r}$$

and

$$-d(M_r)/d(M) = r/2 \cdot \delta^{5/2} k_i^{3/2} (M)^{(r-3)/2} \{ (M)^{1/2} + \delta k_i^{1/2} \}^{-r}$$

This may be integrated by changing to a variable  $\phi = (M)^{-1/2}$ , giving readily:

$$(M_r) = \frac{r \delta^2 k_i}{(r-1)} \left[ \{ 1 + \delta (k_i/(M)_0)^{1/2} \}^{1-r} - \{ 1 + \delta (k_i/(M))^{1/2} \}^{1-r} \right]$$

The weight average chain length can be obtained and is given by:

$$\nu_w = \frac{2}{\delta k_i^{1/2}} \frac{\{ (M)_0^{3/2} - (M)^{3/2} \}}{\{ (M)_0 - (M) \}}$$

*Second Order Initiation.*—For the disproportionation reactions the equations may be written down, namely:

$$-d(M)/dt = (M)^2 \delta^{-1} k_i^{1/2}$$

and

$$\nu_n = \delta^{-1} \cdot k_i^{-1/2} = \bar{\nu}_n$$

Here it is worth emphasizing particularly that the number average chain-length is independent of monomer concentration. Considering the disproportionation reaction first we have:

$$\begin{aligned} d(M_r)/dt &= k_{m_r}(P_r) \sum_{r=1}^{\infty} k_{m_r}(P_r) \\ &= \delta k_i^{3/2} (M)^2 (1 + \delta k_i^{3/2})^{1-r} \end{aligned}$$

Therefore:

$$(M_r) = \delta^2 k_i (1 + \delta k_i^{1/2})^{1-r} \{ (M)_0 - (M) \}$$

and

$$\nu_w = 2 \delta^{-1} \cdot k_i^{1/2}$$

If the chains end by combination the resulting equations are equally simple.

As before:

$$d(M_r)/dt = \frac{1}{2} \sum k_{m\alpha}(P_x) \cdot k_{m_{r-x}}(P_{r-x})$$

therefore

$$(M_r) = \frac{r-1}{2} \cdot \frac{\delta^3 k_i^{3/2}}{(1 + \delta k_i^{1/2})^{r-2}} \{ (M)_0 - (M) \}$$

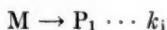
Adopting the methods employed above, the value of  $\lambda_w$  may be found by summing the appropriate series, and is given by:

$$\bar{\nu}_w = 3\delta^{-1} \cdot k_i^{-1/2}$$

*Nonstationary Chains.*—The discussion above has been confined to reactions in which the lifetime of the growing polymer is short compared with the reaction time, so that the stationary state method may be employed to calculate the concentrations of the active polymers. There are, however, reactions in which the lifetime of the active polymer is very long—of the order of days and weeks<sup>3</sup>. It may be noted that this cannot occur in a purely gaseous homogeneous system, for the polymer is deposited on the walls by diffusion and sedimentation within a matter of seconds at atmospheric pressure for normal reactions. This restriction is, of course, removed in liquid phase reactions or reactions occurring on or in the solid polymer itself, i.e., the growth polymethacrylate or polychloroprene.

Quantitative data are practically nonexistent about such reactions, and it is therefore impossible to formulate how the reactivity varies with molecular size. What evidence there is in the case of methacrylate and of chloroprene would indicate that no important change in reactivity occurs over a wide range of sizes. On the other hand, there is every reason to suppose that the velocity coefficients should decrease with increasing molecular size, owing to simple geometrical considerations. We may therefore consider very briefly two extreme cases, (1) coefficients independent of size, (2) coefficients decreasing in magnitude according to some simple law that is tractable as far as this kind of analysis is concerned.

(1) *Velocity Coefficient Independent of Molecular Size.*—The important principle involved is that we may ignore completely any termination reaction and consider only initiation and propagation of the chains. The sequence of events for first order initiation is:



If (P) is for convenience written as  $\sum_{r=1}^{\infty} (P_r)$ , then:

$$d(P)/dt = k_i(M) \quad \text{and} \quad -d(M)/dt = k_p(M)(P)$$

Therefore:

$$-d(P)/d(M) = k_i/k_p(P),$$

whence:

$$(P) = (2k_i/k_p)^{1/2} \{ (M)_0 - (M) \}^{1/2}$$

and

$$-d(M)/dt = (2k_i/k_p)^{1/2} (M) \{ (M)_0 - (M) \}^{1/2}$$

Thus the reaction does not attain maximum rate until some considerable amount of monomer has disappeared. By differentiation of the rate expression this can be shown to occur when  $(M) = 2/3(M)_0$ . The number average is

simply given by  $\bar{\nu}_n = \{(M)_0 - (M)\}/(P) = (k_p/2k_i)^{1/2}\{(M)_0 - (M)\}^{1/2}$ , and the final chain length by:

$$\bar{\nu}_{n\infty} = \{(M)_0/2\alpha\}^{1/2}$$

where  $\alpha = k_i/k_p$ .

To calculate the distribution function the device used by Dostal and Mark may be employed, writing:

$$z = k_p \int_0^t (M) dt$$

$$d(P_1)/dz = k_i/k_p - (P_1)$$

and

$$d(P_r)/dz = (P_{r-1}) - (P_r)$$

which may be integrated successively to give:

$$(P_r) = \alpha e^{-z} \sum_{x=r}^{\infty} \frac{z^x}{x!}$$

$z$  can be shown to be given by:

$$(M)_0 - (M) = \alpha z + 1/2\alpha z^2$$

*Variable Steric Factor, First Order Initiation.*—The simplest possible assumption is made, namely, that  $k_{pr} = k_p/r$ . It is necessary to obtain the distribution function as a preliminary to the rate equation, since we now have:

$$-d(M)/dt = k_p(M) \sum_{r=1}^{\infty} (P_r)/r$$

This may be done by employing the function  $z$  when we have:

$$d(P_1)/dz = k_i/k_p - (P_1)$$

$$d(P_r)/dz = (P_{r-1})(r-1)^{-1} - (P_r)r^{-1}$$

By successive integrations the solution is found to be:

(a)  $r$  even

$$(P_r) = r \cdot k_i/k_p \cdot \left\{ 1 + \frac{e^{-z}}{0!(r-1)!} - \frac{2^{r-1}e^{-z/2}}{1!(r-2)!} + \frac{3^{r-1}e^{-z/3}}{2!(r-3)!} \cdots - \frac{r^{r-1}e^{-z/r}}{(r-1)!0!} \right\}$$

(b)  $r$  odd

$$(P_r) = r \cdot k_i/k_p \cdot \left\{ 1 - \frac{e^{-z}}{0!(r-1)!} + \frac{2^{r-1}e^{-z/2}}{1!(r-2)!} \cdots - \frac{r^{r-1}e^{-z/r}}{(r-1)!0!} \right\}$$

This series is best evaluated arithmetically. Further:

$$(M)_0 - (M) = \sum_{r=1}^{\infty} r(P_r)$$

so that  $(M)_0 - (M)$  and  $-d(M)/dt$  can also be obtained arithmetically. A plot of  $-d(M)/dt$  against  $(M)$  shows a curve with a maximum occurring at a point which depends on the value of  $k_i/k_p$ .

It is also found that a plot of  $\log \{(M)_0 - (M)\}$  against  $\log z$  appears to be asymptotic to the line:

$$(M)_0 - (M) = z^{3/2}$$

which should hold for large values of  $z$ , and thus for reactions leading to long

chains. Under these conditions we obtain:

$$-d(M)/dt = 3/2 \cdot k_i^{2/3} k_p^{1/3} (M) \{ (M)_0 - (M) \}^{1/3}$$

$$(M)/(M)_{0_{\max.}} = 0.75$$

and

$$\bar{v} = (k_p/k_i)^{1/3} \{ (M)_0 - (M) \}^{1/3}$$

## APPLICATION OF KINETIC ANALYSIS

Having derived the equations connecting velocity of polymerization chain-length, distribution of molecular sizes with concentrations of monomer it is now pertinent to enquire how these equations may be applied to elucidate reaction mechanism. The quantities which can be measured in a polymerization process are: (1) the concentration of the monomer and its rate of disappearance; (2) the rate of initiation and the quantum yield, if photochemical; (3) the average chain length, and (4) the distribution of molecular size in the polymer. For convenience, therefore, the velocity and chain-length equations are brought together in Table I so that it may be seen at once how the various

TABLE I  
VELOCITY AND CHAIN-LENGTH FUNCTIONS

Deactivation mechanism	Initiation		
	Photochemical	1st Order	2nd Order
Spontaneous			
$-d(M)/dt$	$f(I)(M)\lambda^{-1}$	$k_i(M)^2\lambda^{-1}$	$k_i(M)^2\lambda^{-1}$
$\bar{v}_n$	$\frac{(M)_0 - (M)}{\lambda \ln \left\{ \frac{(M)_0 + \lambda}{(M) + \lambda} \right\}}$	$\frac{(M)_0 - (M)}{\lambda \ln \left\{ \frac{(M)_0 + \lambda}{(M) + \lambda} \right\}}$	$\frac{(M)_0 - (M)}{\lambda \ln \left\{ \frac{(M)_0 + \lambda}{(M) + \lambda} \right\}}$
$\bar{v}_w$	$\frac{(M)_0 + (M)}{\lambda}$	$\frac{(M)_0 + (M)}{\lambda}$	$\frac{(M)_0 + (M)}{\lambda}$
Monomer			
$-d(M)/dt$	$f(I)\lambda^{-1}$	$k_i(M)\lambda^{-1}$	$k_i(M)^2\lambda^{-1}$
$\bar{v}_n = \frac{1}{2}\bar{v}_w$	$\lambda^{-1}$	$\lambda^{-1}$	$\lambda^{-1}$
Mutual (dispropn.)			
$-d(M)/dt$	$f(I)^{1/2}(M)\delta^{-1}$	$k_i^{1/2}(M)^{3/2}\delta^{-1}$	$k_i^{1/2}(M)^2\delta^{-1}$
$\bar{v}_n$	$\frac{(M)_0 - (M)}{\delta f(I)^{1/2} \ln \left\{ \frac{(M)_0 + \delta f(I)^{1/2}}{(M) + \delta f(I)^{1/2}} \right\}}$	$\frac{(M)_0^{1/2} + (M)^{1/2}}{2\delta k_i^{1/2}}$	$\delta^{-1}k_i^{-1/2}$
$\bar{v}_w$	$\frac{(M)_0 + (M)}{\delta f(I)^{1/2}}$	$\frac{2 \{ (M)_0^{3/2} - (M)^{3/2} \}}{\delta k_i^{1/2} \{ (M)_0 - (M) \}}$	$2\delta^{-1}k_i^{-1/2}$
None ( $k_p$ const.)			
$-d(M)/dt$	—	$(2k_i k_p)^{1/2}(M) \{ (M)_0 - (M) \}^{1/2}$	$(k_i k_p)^{1/2}(M) \{ (M)_0^2 - (M)^2 \}^{1/2}$
$\bar{v}_n$	—	$\{ \{ (M)_0 - (M) \} / \alpha 2 \}^{1/2}$	$\{ \{ (M)_0 - (M) \} / \alpha \}^{1/2}$
None ( $k_p = k_p/r$ )			
$-d(M)/dt$	—	$\frac{3}{2}(M) [k_i^2 k_p \{ (M)_0 - (M) \}]^{1/3}$	—
$\bar{v}_n$	—	$\{ \{ (M)_0 - (M) \} / \alpha \}^{1/3}$	—

\* Combination reaction.

modes of initiation and termination affect the order of the reaction. From an examination of the Table, it will be observed that the order serves to dis-

criminate between the mechanisms except in the following cases: second order initiation and monomer termination, second order initiation and mutual destruction. An examination of the variation of chain length with temperature would probably facilitate a choice. Since  $\lambda = k_t/k_p$  its temperature coefficient is most probably of the order of a few thousand calories, whereas  $\delta k_i^{1/2}$  probably possesses a temperature coefficient corresponding to an energy of activation of at least 10 k. cal., since the energy of activation is certainly not less than 20 k. cal.

Curve I for photo, 1st order and 2nd order initiation with spontaneous termination.  $\lambda/(M)_0 = 5 \times 10^{-3}$ . Photo initiation with mutual destruction by disproportionation  $\delta f(1) = 5 \times 10^{-3}$ .

Curve II.—Any type of initiation, monomer termination  $\lambda = 10^{-2}$ . 1st order initiation, mutual destruction, combination  $\delta k_i^{1/2}/(M)_0^{1/2} = 10^{-2}$ . 2nd order initiation, mutual destruction, disproportionation  $\delta k_i^{1/2} = 10^{-2}$ .

Curve III.—Photo initiation, mutual destruction, combination

$$\delta f(1)^{1/2} = 10^{-2}.$$

Curve IV.—2nd order initiation, mutual destruction, combination

$$\delta k_i^{1/2} = 2 \times 10^{-2}.$$

In the cases where there is no deactivation, the rate equations bear a similarity to each other and are slightly complicated so that it is not immediately evident how discrimination could be accomplished. To make the distinction clearer, therefore, the three rate equations are plotted as a function of  $(M)$  in Figure 1. Even then it is extremely difficult to find the point of

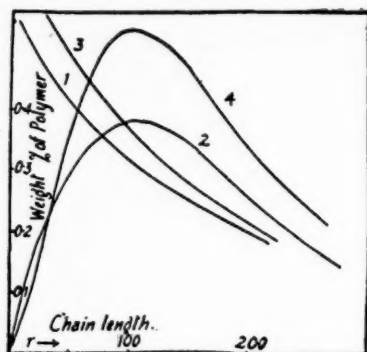


FIG. 1.—Molecular-weight distribution curves for various types of polymerization reactions.

inflection in the  $(M) - t$  curve with precision, and hence kinetic analysis here reaches its limit. But we must note that it might be possible to discriminate by measuring the chain length, since with first order initiation, the chain length will be independent of the initial concentrations (since  $\alpha \sim (M)_0$ ), and with second order initiation the chain length will be proportional to the square root of  $(M)$ .

For convenience the various distribution functions are collected in Table II. The distribution curves for the stationary chains shown in Figure 2 fall essentially into two classes, *viz.*, those exhibiting a maximum which occurs at the same value as the average chain length itself, and those which exhibit a con-

TABLE II  
 DISTRIBUTION ON FUNCTIONS

Initiation mechanism	Termination mechanism	$w_r$ (at the end of reaction)
Any	Spontaneous	$\frac{\lambda}{(M)_0 \{1 + \lambda/(M)_0\}^r}$
Any	Monomer	$\lambda r(1 + \lambda)^{-r}$
Photo	Mutual (dispropn.)	$\frac{\delta f(I) \{1 + \delta f(I)/(M)_0\}^{-r}}{(M)_0}$
Photo	Mutual (combn.)	$\frac{\delta^2 f(I)}{2(M)_0^2} \cdot \frac{\{r + (M)_0 \delta f(I)^{1/2}\}}{\{1 + \delta f(I)^{1/2}/(M)_0\}^r}$
1st	Mutual (combn.)	$\frac{r \delta^2 k_i}{(M)_0 \{1 + \delta k_i^{1/2} (M)_0^{-1/2}\}^r}$
2nd	Mutual (dispropn.)	$r \delta^2 k_i (1 + \delta k_i)^{-r}$
2nd	Mutual (combn.)	$\frac{1}{2} \cdot r^2 \delta^3 k_i^{3/2} (1 + \delta k_i^{1/2})^{-r}$
1st	None	$\frac{\alpha r}{(M)_0} e^{-z} \sum_{z=r}^{\infty} \frac{z^n}{z!}$

tinuous decrease of the fraction of the polymer with a given weight as this weight increases. The rapidity with which curves I and III descend shows that, should the reaction follow these mechanisms, the proportion of small polymers is large and should be detectable experimentally. For the non-stationary reaction, Dostal and Mark have shown that the distribution takes

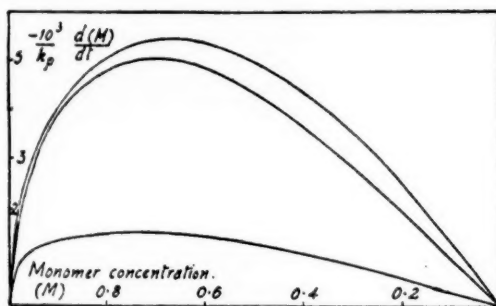


Fig. 2.—Velocity-monomer concentration curves for nonstationary reactions. I. 1st order  $k_p r = \text{const.}$  II. 2nd order  $k_p r = \text{const.}$  III. 1st order  $k_p r = kr^{-1}$ .  $(M)_0 = 1 \cdot \alpha = 10^{-4}$ .

on another quite characteristic form, in which the short chain products are present in very small amounts.

### CATALYZED POLYMERIZATION

Catalyzed reactions do not differ fundamentally from noncatalyzed ones, and the equations already given may be applied with slight modification. It has been shown that in a stationary reaction, catalytic initiation may be kinetically of the first or second order, in which case the equations given in columns three and four of Table I apply *mutatis mutandis*. If the catalyst is stable, i.e., does not undergo any side reaction leading to its removal, it is only



necessary to replace  $k_i$  by  $k_e(C)_0$  where  $(C)_0$  is the concentration of catalyst added initially. If the catalyst is unstable its concentration at time  $t$  is given by:

$$(C) = (C)_0 e^{-k_e t}$$

and the appropriate substitution is:

$$k_i = k_e(C)_0 e^{-k_e t}$$

If the catalyst added reacts slowly with the monomer to form a complex of relatively long life, the overall rate of reaction will show an initial period of acceleration, and the above equations cannot be applied<sup>4</sup>.

### EFFECT OF INHIBITORS

If an inhibitor is present in sufficient quantity to overshadow the normal termination mechanism, then the kinetics reduce formally to the case of spontaneous termination, except that  $\lambda$  must be replaced by  $\beta(X)$ . If the inhibitor concentration is too small for this to hold, the equations become more complicated and, in the case where termination occurs normally by mutual deactivation, are not generally soluble. In Table III are presented the kinetic

TABLE III  
RATE AND CHAIN LENGTH OF INHIBITED POLYMERIZATION  
(NORMAL TERMINATION BY MONOMER)

	Photochemical	1st Order
(a) Stable Inhibitor		
$-d(M)/dt$	$\frac{f(I)(M)}{\lambda(M) + \beta(X)}$	$\frac{k_i(M)^2}{\lambda(M) + \beta(X)}$
$\bar{v}_n$	$\frac{(M)_0 - (M)}{\lambda\{(M)_0 - (M)\} + \beta(X) \ln \left\{ \frac{(M)_0 + \beta(X)}{(M) + \beta(X)} \right\}}$	
(b) Unstable Inhibitor		
$-d(M)/dt$	$\frac{f(I)(M)}{\lambda(M) + \beta(X_0)\{(M)/(M)_0\}^\beta}$	$\frac{k_i(M)^2}{\lambda(M) + \beta(X_0)\{(M)/(M)_0\}^\beta}$

equations derived on the assumption that the normal termination mechanism is by collision with the monomer. Two cases are distinguished: (1) in which the inhibitor is not destroyed in the process of terminating a chain ("stable inhibitor"); and (2) in which a molecule of inhibitor disappears for every chain terminated.

### SUMMARY

A general treatment of the kinetics of polymerization reactions is given to cover the two extreme conditions in which the lifetime of chain growth is (1) small, and (2) large compared with the half life of the monomer. Case (1) is considered on the basis of the assumption that the velocity coefficients do not depend on molecular size. Case (2) is considered for propagation coefficients which are on the one hand independent, and on the other hand dependent on molecular size. In addition, the distribution of molecular sizes is computed in those cases where the mathematical difficulties are not insurmountable.

The application of these results to the analysis of polymerization reactions is discussed.



The work described in this paper was completed when war broke out, and was to have been published as part of a book on polymerization processes. In view of the interest and development in these matters, it was felt desirable to give this account of these ideas now.

## REFERENCES

- <sup>1</sup> A summary of the more common cases is given by Mark and Raff ("High Polymers", Interscience Publishers, New York, Vol. 3).
- <sup>2</sup> No well defined cases of spontaneous termination have yet been discovered.
- <sup>3</sup> Melville, *Proc. Roy. Soc. London* **163A**, 511 (1937); Bolland and Melville, *Proc. Rubber Tech. Conf. London*, **1938**, p. 239.
- <sup>4</sup> A full discussion of this problem in relation to the catalyzed polymerization of vinyl acetate has been given by Cuthbertson, Gee and Rideal (*Proc. Roy. Soc. London* **170A**, 300 (1939)).

# THE INTERACTION BETWEEN RUBBER AND LIQUIDS \*

## V. THE OSMOTIC PRESSURES OF POLYMER SOLUTIONS IN MIXED SOLVENTS

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### INTRODUCTION

The interpretation of the osmotic pressures of polymer solutions in single solvents has been discussed recently by a number of authors<sup>1</sup>. By making use of the thermodynamic relationship between the osmotic pressure ( $\Pi$ ) in a solvent of molar volume  $V_0$  and the Gibbs' free energy of dilution ( $\Delta G_0$ ) of the solution, the problem is reduced to the statistical calculation of  $\Delta G_0$ :

$$\Pi V_0 \approx - \Delta G_0 \quad (1)$$

(valid for dilute solutions).

The free energy of mixing of linear flexible polymers, *e.g.*, rubber, with liquids has been calculated by computing the number of configurations of the system on a lattice, each point of which can accommodate either a solvent molecule or a "segment" of the chain<sup>2</sup>. The solution of this problem has been obtained in two ways. (1) If there is no change of energy, mixing will be random, and the increase of entropy can be calculated. The free energy is then obtained by adding a heat term, assuming that this will not seriously affect the entropy. (2) More recently, Orr<sup>3</sup> and Guggenheim<sup>4</sup> have shown how to calculate the free energy directly, allowing for the effect of nonrandom mixing arising from finite energy changes. For small heats of mixing, the results of the second method are not very greatly different from those of the first, which we use in the present paper on account of their greater simplicity.

Miller's expression for the entropy of dilution  $\Delta S_0^r$  is:

$$\Delta S_0^r = -R \left[ \ln(1 - v_r) - \frac{Z}{2} \ln \left\{ 1 - \frac{2v_r}{Z} \left( 1 - \frac{1}{n} \right) \right\} \right] \quad (2)$$

where  $v_r$  is the volume fraction of polymer in the mixture,

$n$  is the number of segments in a polymer chain,

$Z$  is the coördination number of the lattice.

For dilute solutions, this reduces to:

$$\frac{\Delta S_0^r}{R} \approx \frac{v_r}{n} + \left( \frac{1}{2} - \frac{1}{Z} \right) v_r^2 \quad (3)$$

\* Reprinted from the *Transactions of the Faraday Society*, Vol. 40, Part 10, pages 463-480, October 1944. For Part IV of the series, see *RUBBER CHEMISTRY AND TECHNOLOGY*, Vol. 16, No. 4, pages 818-833, October 1943.

The heat of dilution  $\Delta H_0^r$  is assumed<sup>1</sup> to be of the form<sup>5</sup>:

$$\Delta H_0^r = \beta V_0 v_r^2 \quad (4)$$

Combining (3) and (4) with (1), and replacing  $v_r$  by  $C/\rho_r$  where  $C$ ,  $\rho_r$  are the concentration and density of the polymer, the osmotic pressure is given by:

$$\frac{\Pi}{C} \approx \frac{RT}{M_r} + \left\{ \left( \frac{1}{2} - \frac{1}{Z} \right) \frac{RT}{V_0} - \beta \right\} \frac{C}{\rho_r^2} \quad (5)$$

where  $M_r$  is the molecular weight of the polymer.

An equation of this form has been used with considerable success, and in particular plots of  $\Pi/C$  against  $C$  for a homologous series of polymers are in general very nearly linear and parallel<sup>6</sup>. Exceptions have been reported<sup>7</sup> in the form of curved plots of  $\Pi/C \sim C$ , and it has also been shown<sup>8</sup> that the values of  $\beta$  required to fit experimental data to Equation (5) are not necessarily exactly equal to those calculated from the heat of dilution (Equation (4)). In view of the crudeness of the model on which the result is based and the neglect of volume changes on mixing, these small discrepancies are not surprising, and the theoretical treatment must be considered very satisfactory. It is the purpose of the present paper to extend the treatment in order to calculate the osmotic pressures of polymer solutions in mixed solvents to a similar approximation.

The problem falls into two parts: (1) the statistical derivation of an expression for the free energy of a ternary mixture of polymer plus two liquids, and (2) the thermodynamic treatment of the osmotic equilibrium between a ternary mixture and a binary mixture of the two liquids. The first of these is included as a special case of Guggenheim's most general formulation of the free energies of mixtures including polymers<sup>4</sup>. We show here how an approximate result may be obtained in a simpler form by making use of the above expressions (Equations (2) and (3)) for the entropy of dilution of a polymer by a single liquid.

*The Free Energy of the Ternary System Rubber + 2 Liquids.* The specification of the composition of a ternary mixture requires two variables. In this paper we use the volume fraction  $v_r$  of the rubber, and the molecular ratio  $p$  of the two liquids. Thus, if  $v_1^r$ ,  $v_2^r$  are the volume fractions of liquids 1 and 2, and  $V_1$ ,  $V_2$  their molar volumes, we have:

$$p \equiv \frac{v_1^r}{v_2^r} \cdot \frac{V_2}{V_1}$$

Writing  $\frac{V_2}{V_1} \equiv l$ , this gives  $v_1^r \equiv \frac{p}{p+l} (1 - v_r)$ ;  $v_2^r \equiv \frac{l}{p+l} (1 - v_r)$ .

Throughout the paper we shall use the superscript  $r$  to denote a phase containing rubber.

The entropy of dilution  $\Delta S_1^r$  of a ternary mixture by pure liquid 1 is readily related to the entropy of dilution  $\Delta S_0^r$  of a binary mixture by pure liquid 1 in the following way. The number of configurations of a fixed number of polymer molecules plus a given number of liquid molecules is independent of whether the latter are all of one kind, so long as their molecular volumes are not widely different. Hence the entropy of mixing of a polymer with two liquids differs from that of the polymer with the same volume of a single liquid only by the entropy of mixing of the liquids with one another. Thus, if  $\Delta S_1^r$  and  $\Delta S_0^r$  are

measured at constant  $v_r$ :

$$\Delta S_1^r = \Delta S_0^r + R \ln \left( \frac{p+1}{p} \right)$$

$$(v_r \text{ constant}) \quad \Delta S_2^r = \Delta S_0^r + R \ln (p+1) \quad (6)$$

If we assume the areas of contact of the three components of a ternary mixture to be proportional to their volume fractions, it is easy to show that the heat of mixing, per cc., is of the form:

$$\Delta E^m = \alpha \frac{pl}{(p+l)^2} (1-v_r)^2 + \frac{\beta p + \gamma l}{p+l} v_r (1-v_r) \quad (7)$$

Neglecting volume changes, the heats of dilution  $\Delta H_1^r$  and  $\Delta H_2^r$  of the mixture by the pure liquids are:

$$\Delta H_1^r = a + bv_r + cv_r^2$$

$$\Delta H_2^r = p^2/l \cdot a - bp \cdot v_r + lcv_r^2 \quad (8)$$

where

$$a \equiv \frac{V_1}{(p+l)^2} \cdot \alpha l^2$$

$$b \equiv \frac{V_1}{(p+l)^2} \{ (\beta - \alpha - \gamma) l^2 + (\beta + \alpha - \gamma) pl \}$$

$$c \equiv \frac{V_1}{(p+l)^2} \{ \gamma l^2 + (\beta - \alpha + \gamma) pl + \beta p^2 \}$$

Combining Equations (6) and (8) gives for the free energies of dilution:

$$\Delta G_1^r = a + bv_r + cv_r^2 - T\Delta S_0^r - RT \ln \frac{p+1}{p}$$

$$\Delta G_2^r = \frac{p^2}{l} \cdot a - pbv_r + lcv_r^2 - T\Delta S_0^r - RT \ln (p+1) \quad (9)$$

Assuming  $\Delta S_0^r$  to be known as a function of  $v_r$ , Equation (9) gives the free energies of dilution in terms of the three constants  $\alpha$ ,  $\beta$ , and  $\gamma$ . These may be related to the heats of mixing (per cc.) of the three possible binary mixtures:

$$\left. \begin{aligned} \Delta E_{1,2}^m &= \alpha v_1 v_2 \\ \Delta E_{1,r}^m &= \beta v_1 v_r \\ \Delta E_{2,r}^m &= \gamma v_2 v_r \end{aligned} \right\} \quad (10)$$

*Osmotic Equilibrium between Ternary and Binary Mixtures.* We now consider the osmotic equilibrium between a ternary mixture of polymer + two liquids and a binary mixture of the two liquids, the phases being separated by a membrane permeable to both liquids, but impermeable to the polymer. Denoting the solvent phase by a superscript  $s$ , the equilibrium conditions are:

$$\left. \begin{aligned} \Delta G_1^r &= \Delta G_1^s \\ \Delta G_2^r &= \Delta G_2^s \end{aligned} \right\} \quad (11)$$

In conformity with the notation employed for the ternary phase we use, as concentration variable for the binary phase, the molecular ratio  $q$  of the two

liquids, so that their volume fractions  $v_1^s$  and  $v_2^s$  are given by  $v_1^s = q/(q + l)$ ;  $v_2^s = l/(q + l)$ . Assuming the "ideal" entropy of mixing, the free energies of dilution of the binary mixture are:

$$\left. \begin{aligned} \Delta G_1^s &= \alpha V_1 \left( \frac{l}{q + l} \right)^2 - RT \ln \left( \frac{q + 1}{q} \right) \\ \Delta G_2^s &= \alpha V_2 \left( \frac{q}{q + l} \right)^2 - RT \ln (q + 1) \end{aligned} \right\} \quad (12)$$

If a small pressure  $\Pi$  is applied to the polymer phase, the free energies  $\Delta G_1^r$  and  $\Delta G_2^r$ , given by Equations (9) will be increased by  $\Pi V_1$ ,  $\Pi V_2$ , respectively. If the two phases are in equilibrium,  $\Pi$  is, by definition, the osmotic pressure of the polymer solution, and may be calculated by inserting values in Equation (11) to give:

$$\left. \begin{aligned} \ln \left( \frac{q + 1}{q} \right) - \frac{\alpha V_1}{RT} \left( \frac{l}{q + l} \right)^2 &= \frac{\Delta S_0^r}{R} + \ln \left( \frac{p + 1}{p} \right) \\ &\quad - \frac{a + bv_r + cv_r^2 + \Pi V_1}{RT} \\ \ln (q + 1) - \frac{\alpha V_2}{RT} \left( \frac{q}{q + l} \right)^2 &= \frac{\Delta S_0^r}{R} + \ln (p + 1) \\ &\quad - \frac{p^2 a - plbv_r + l^2 cv_r^2 + \Pi V_2 l}{lRT} \end{aligned} \right\} \quad (13)$$

These equations give the complete relationship between the four variables  $p$ ,  $q$ ,  $v_r$ ,  $\Pi$ , any two of which may be fixed arbitrarily<sup>9</sup>. In particular, if we define completely the composition of the solution ( $p$ ,  $v_r$ ) we fix both the osmotic pressure and the composition of the solvent.

No algebraic solution of these equations appears to be possible, but if  $v_r$  is small, we may obtain an approximate solution as follows. A new variable  $r$  is defined as  $(q/p - 1)$  and Equation (13) written in the form:

$$\left. \begin{aligned} \ln \left\{ \frac{1 + pr/(p + 1)}{1 + r} \right\} + \frac{\alpha V_1}{RT} \left( \frac{l}{p + l} \right)^2 \left\{ 1 - \left( 1 + \frac{pr}{p + l} \right)^{-2} \right\} \\ = \frac{\Delta S_0^r}{R} - \frac{bv_r + cv_r^2 + \Pi V_1}{RT} \\ \ln \left\{ 1 + \frac{pr}{p + 1} \right\} = \frac{\alpha V_1 l}{RT} \left( \frac{p}{p + l} \right)^2 \left\{ \left( \frac{1 + r}{1 + \frac{pr}{p + l}} \right)^2 - 1 \right\} \\ = \frac{\Delta S_0^r}{R} + \frac{pbv_r - clv_r^2 - \Pi V_2}{RT} \end{aligned} \right\} \quad (14)$$

Now it is physically obvious that  $r \rightarrow 0$  as  $v_r \rightarrow 0$ , so that, for small  $v_r$ , all functions of  $r$  in (14) may be expanded, retaining no powers of  $r$  higher than the first. This gives:

$$\left. \begin{aligned} r \left\{ \frac{1}{p + 1} - \frac{2\alpha V_1}{RT} \cdot \frac{l^2 p}{(p + l)^3} \right\} &\approx - \frac{\Delta S_0^r}{R} + \frac{bv_r + cv_r^2 + \Pi V_1}{RT} \\ pr \left\{ \frac{1}{p + 1} - \frac{2\alpha V_1}{RT} \cdot \frac{l^2 p}{(p + l)^3} \right\} &\approx \frac{\Delta S_0^r}{R} + \frac{pbv_r - clv_r^2 - l\Pi V_1}{RT} \end{aligned} \right\} \quad (15)$$

whence

$$\Pi \approx \frac{p+1}{p+l} \cdot \frac{T\Delta S_0^r}{V_1} - \frac{\beta p^2 + (\gamma - \alpha + \beta)pl + \gamma l^2}{(p+l)^2} \cdot v_r^2 \quad (16)$$

We may now substitute for  $\Delta S_0^r$  from Equation (3), but the precise significance to be attached to  $n$  requires some consideration. For the two pure liquids  $n$  will be  $V_r/V_1$ ,  $V_r/V_2$ , respectively, where  $V_r$  is the molar volume of the polymer. To be consistent with both of these, we define  $n$  for the mixed liquid by:

$$n = \frac{v_1^r + v_2^r}{v_1^r V_1 + v_2^r V_2} \cdot V_r = \frac{p+1}{p+l} \cdot \frac{V_r}{V_1} \quad (17)$$

Combining Equations (3), (16) and (17), and replacing  $v_r$  by  $C/\rho_r$ , gives finally:

$$\frac{\Pi}{C} \approx \frac{RT}{M_r} + \left\{ \left( \frac{1}{2} - \frac{1}{Z} \right) \frac{p+1}{p+l} \cdot \frac{RT}{V_1} - \frac{\beta p^2 + (\gamma - \alpha + \beta)pl + \gamma l^2}{(p+l)^2} \right\} \frac{C}{\rho_r^2} \quad (18)$$

It follows that:

$$\lim_{C \rightarrow 0} \left( \frac{\Pi}{C} \right) = \frac{RT}{M_r} \quad (19)$$

i.e., van't Hoff's law holds at infinite dilution, just as in the case of solutions in single liquids.  $\Pi/C$  should still be a linear function of  $C$ , but the slope now depends on the composition of the mixture, and on the values of  $\alpha$ ,  $\beta$ ,  $\gamma$ .

It has been shown experimentally<sup>10</sup> that by using a mixture of solvent and nonsolvent in suitable proportions, it is possible to prepare polymer solutions which obey van't Hoff's law at a single temperature, i.e.,  $\frac{\partial(\Pi/C)}{\partial C} = 0$ . Inserting this condition in Equation (18), and writing  $\zeta \equiv \left( \frac{1}{2} - \frac{1}{Z} \right) \frac{RT}{V_1}$ , we obtain a quadratic in  $p$ :

$$p^2(\zeta - \beta) + p\{\alpha + l(\zeta - \beta) + (\zeta - l\gamma)\} + l(\zeta - l\gamma) = 0 \quad (20)$$

If solutions in liquid 1 have osmotic pressures greater than  $\frac{RT}{M_r} \cdot C$ , we must have  $\zeta > \beta$ . If liquid (2) is not a solvent,  $\zeta < \gamma l$  (cf. next paper). With these restrictions it can be shown that Equation (20) has always one positive root, i.e., it is always possible to find a mixture of solvent and nonsolvent which will give solutions obeying van't Hoff's law at a single temperature.

*Distribution of Liquids between the Two Phases.* Substituting for  $\Pi$  from (16) in (15), we find for  $r$ :

$$r \approx \frac{(1-l)(p+l)^2 T \Delta S_0^r + \{(\beta - \gamma)(p+l)^2 + \alpha(p^2 - l^2)\} V_2 v_r}{\frac{(p+l)^3}{p+1} \cdot RT - 2\alpha p l V_2} \quad (21)$$

If the three components all mix athermally, i.e.,  $\alpha = \beta = \gamma = 0$ , this reduces to:

$$r \approx (1-l) \frac{p+1}{p+l} \cdot \frac{\Delta S_0^r}{R}$$

which is not zero unless  $l = 1$ , i.e., the two liquids have equal molar volumes.

For  $v_r = 0.01$ , we have, however,  $r \approx 4 \times 10^{-5} (1 - l)$ , so the molar ratios of the liquids on the two sides of the membrane would only differ by about  $10^{-3}$  per cent. If  $\alpha, \beta, \gamma$  are all fairly large,  $r$  may well be of the same order as  $v_r$ .

*The Practical Use of Mixed Liquids in Osmotic Measurements.* In a recent paper, Wall<sup>11</sup> has called attention to the fact that in an osmotic equilibrium of the kind considered here there must generally be an uneven distribution of the two liquids on opposite sides of the membrane, and has suggested that this might lead to experimental difficulties. The present author has used benzene-methyl alcohol mixtures as rubber solvents without observing any trouble of the kind envisaged by Wall, nor is any difficulty reported by Dobry<sup>12</sup>. In all cases which have been examined, mixed solvents have given the same limiting value of  $\Pi/C$  as single liquids. At the same time, it could scarcely be maintained that the solvent distribution throughout the two cells of the osmometer reaches equilibrium by osmosis and diffusion within the time required for an osmotic pressure measurement. This apparent contradiction suggests that the osmotic equilibrium is set up between two very thin layers in immediate contact with the membrane. Adjustment of the solvent distribution will occur mainly on the solvent side of the membrane, owing to the high viscosity of the polymer solution, so that the osmotic pressure finally obtained may be properly described as that of the solution as made up.

#### SUMMARY

An expression is obtained for the free energy of dilution of a ternary mixture of polymers + two liquids by one of the liquids. This is used to consider the osmotic equilibrium between a solution of a polymer in a mixture of two liquids, and a second phase containing only the two liquids. It is shown that the osmotic behavior of the ternary solution is very similar to that of a polymer in a single liquid, and in particular that van't Hoff's law holds at infinite dilution. The distribution of the two liquids between solvent and solution is also calculated. The experimental difficulties involved in the use of mixed solvents are discussed.

## VI. SWELLING AND SOLUBILITY IN MIXED LIQUIDS

### INTRODUCTION

The statistical thermodynamical treatment of the solubility and swelling of polymers in single liquids has been successful in interpreting the main features of the experimental results<sup>13</sup>. This method has not so far been applied to polymers in mixed liquids, except by treating the mixture as a single liquid having properties intermediate between those of its components<sup>14</sup>. That such an assumption cannot be generally valid is evident from the existence of numerous examples of pairs of liquids which individually are not solvents for a given polymer, but which dissolve it when used in admixture, e.g., nitrocellulose in ethyl alcohol + ether<sup>15</sup>, glyptal in *n*-butyl acetate + ethyl alcohol<sup>16</sup>, polystyrene in acetone + *n*-propyl laurate<sup>17</sup>. Another closely related phenomenon is the increased ease of solution of natural rubber in hexane on adding small quantities of alcohols or ketones—themselves nonsolvents<sup>18</sup>. Where any explanation of these observations has been attempted, it has been in terms of



the solvation of different parts of the polymer molecule by the two components of the mixture<sup>19</sup>. Now, while this view may sometimes be justified, it by no means follows that it is invariably or even usually true. Since it has been found necessary to abandon the view that solvation is generally the cause of rubber dispersion, it is natural to enquire whether the treatment found so successful for single liquids can be extended to mixed liquids, and if so, whether it can account for the existence of phenomena such as have been mentioned above. It will be shown in this paper that the problem can in fact be so treated, and at least a semiquantitative theory developed.

It is worthwhile to contrast the assumptions involved in the present theory with those of the solvation hypothesis, and to consider their probable validity. The polymer molecule is treated as a flexible chain of segments, each of which can be interchanged with a molecule of either liquid, the system thus arranging itself in a random way by virtue of the thermal motions of its components. All intermolecular forces are assumed to be nonlocalized, and in particular the force field around the polymer chain is treated as uniform. It is obvious that this is not strictly true, and it is especially false in the case of copolymers of the Buna-N type, in which highly polar groups are separated by relatively long hydrocarbon chains. The solvation hypothesis goes to the other extreme by directing attention exclusively to localized forces. The success with which the statistical thermodynamic method accounts for the swelling of even synthetic rubbers in single liquids encourages the belief that it can be extended to mixed liquids without any radically new assumptions being introduced.

#### LIMITED SWELLING

The swelling of cross-linked polymers, *e.g.*, vulcanized rubbers, or of linear polymers of high molecular-weight in nonsolvents may be regarded as an osmotic phenomenon. The final equilibrium swelling is in fact determined by an osmotic equilibrium between the polymer phase (solution) and the liquid, the polymer itself acting as the semipermeable membrane. The osmotic pressure is of course zero, and the problem is thus a special case of the general one considered in the previous paper. The conditions for equilibrium between the two phases are given by putting  $\Pi = 0$  in Equation (13) of that paper<sup>20</sup>. As we have noted, no general algebraic solution is possible, but the problem is greatly simplified for the special case that the two liquids form ideal mixtures with one another, so that  $\alpha = 0$ . This case is of considerable intrinsic interest, since it would seem to be a necessary condition of the assumption that the mixture behaves as a single liquid having properties intermediate between those of its components. If  $\alpha = 0$ ,  $\Pi = 0$ , (13) may be written:

$$\begin{aligned} 1 + \frac{1}{q} &= \left( 1 + \frac{1}{p} \right) \exp \left( \frac{\Delta S_0 r}{R} - \frac{bv_r + cv_r^2}{RT} \right) \\ 1 + q &= (1 + p) \exp \left( \frac{\Delta S_0 r}{R} + \frac{pbv_r - cv_r^2}{RT} \right) \end{aligned} \quad (22)$$

It is easily shown, inserting values of  $b$  and  $c$ , that:

$$q = p \exp \left[ \frac{V_l v_r}{RT(p + l)} \{ l(p + 1)(\beta - \gamma) + (1 - l)(\beta p + \gamma l)v_r \} \right] \quad (23)$$

This expression for the distribution of the liquids between the two phases is

further simplified if  $V_1 = V_2$  (i.e.,  $l = 1$ ) or  $\beta = \gamma$ :

$$(i) \quad V_1 = V_2; \ln(q/p) = \frac{V_1 v_r}{RT} (\beta - \gamma) \quad (23')$$

$$(ii) \quad \beta = \gamma; \ln(q/p) = \frac{\beta v_r^2}{RT} (V_1 - V_2) \quad (23'')$$

These equations express conclusions which might have been anticipated physically, but which are only valid if  $\alpha = 0$ :

(1) Of two liquids of equal molecular volume, the one whose heat of mixing (per cc.) with the polymer is the smaller will be preferentially absorbed.

(2) Of two liquids whose heats of mixing (per cc.) with the rubber are identical, the one of smaller molecular volume will be preferentially absorbed. These may be combined to yield the obvious conclusion that the better swelling agent is preferentially absorbed.

The effect of a positive value of  $\alpha$  has been determined by arithmetical solution of Equations (13) simplified by making  $\beta = \gamma$ ,  $l = 1$ . It is then found that the larger  $\alpha$  is made, the more nearly does the liquid ratio in the polymer phase tend to unity, for any ratio in the swelling medium, i.e.,  $p \rightarrow 1$ , and is always nearer to 1 than is  $q$ . In general, therefore, when  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $l$  have any values, the distribution will be determined by the balance between two opposing tendencies: (1) for the better swelling agent to be preferentially absorbed, and (2) for the liquid composition of the ternary phase to be more uniform than that of the binary.

Elimination of  $q$  between (23) and the second line of Equation (22) can be seen to give a somewhat complex expression for  $p$ . A very much simpler approximate solution is obtained if  $q \approx p$ , which will generally be true when  $\alpha = 0$  (cf. Equations 23' and 23''). The exponential terms of (22) and (23) may then be expanded as  $e^x \approx 1 + x$ , whereby we obtain:

$$\frac{T\Delta S_0^r}{V_1 v_r^2} \approx \frac{\beta p + \gamma l}{p + 1} \quad (24)$$

At constant  $T$ , the left-hand side is a monotonic function of  $v_r$ . Its values for the pure liquids are  $\gamma l$  (at  $p = 0$ ) and  $\beta$  (at  $p = \infty$ ); for any mixture its value lies between these limits.

It follows that, if two liquids mix ideally, the swelling power of any mixture of them lies between their separate swelling powers. Where swelling is observed outside these limits it is to be attributed (on this theory) to interaction between the two liquids.

If  $\alpha \neq 0$ , Equations (13) can only be solved arithmetically; some examples will be given in a later section. We may anticipate these results by noting that they show enhanced swelling power of mixtures to be associated with large values of  $\alpha$ .

#### CRITICAL SOLUBILITY LIMITS

If a nonsolvent is added to a polymer solution, a certain critical amount will be required to cause precipitation to commence. Brønsted and Volqvartz<sup>17</sup> showed experimentally that, in the case of polystyrene of sufficiently high molecular weight, this liquid composition formed a sharp line of demarcation between perfect solvents and nonsolvents. Mixtures slightly richer in solvent were miscible in all proportions with the polystyrene; poorer mixtures pro-

duced no perceptible dispersion. Similar critical phenomena are found with single liquids<sup>21</sup> when the temperature is varied, and have been shown<sup>13</sup> to find a natural explanation in the very large temperature coefficient of solubility predicted by the statistical thermodynamic theory. The exact treatment of solubility problems requires us to consider the equilibrium between two ternary phases. This we hope to do in a later paper, but the algebra becomes so involved that only certain special problems will be considered. It is possible, however, to give a very much simpler treatment of the critical solubility limits for polymers of very high molecular weight, as follows.

Let us consider the osmotic pressure of a very dilute polymer solution in a mixture of solvent and nonsolvent. If the solution is sufficiently dilute the solvent-nonsolvent ratios on the two sides of the membrane are not sensibly different (*cf.* previous paper). Now suppose the composition of the mixture to be gradually changed by adding nonsolvent, equilibrium being maintained. The osmotic pressure falls, according to Equation (18), but before it reaches zero, the solution separates into two phases, the new one containing a much higher polymer concentration and—in general—a different solvent nonsolvent ratio. It is evident that the lower the concentration of the solution, the closer the osmotic pressure approaches to zero before precipitation occurs. Now Brønsted and Volqvartz' observations show that the precipitation point is independent of the polymer concentration for polymers of sufficiently high molecular weight. It follows that there cannot be any significant difference between the liquid composition at (1), the critical solubility point, and (2) the point at which  $\Pi = 0$ . Hence, the critical solubility limits for polymers of infinite molecular weight can be obtained by finding the conditions for the osmotic pressure of a dilute solution to be zero.

Putting  $\Pi = 0$ ,  $M_r \rightarrow \infty$  in Equation (18) we see that the condition for the critical solubility limit at infinite molecular weight is precisely the condition that van't Hoff's law shall hold for polymers of finite molecular weight, and is given therefore by Equation (20). The validity of this method may be illustrated by reference to the solubility and osmotic pressure of natural rubber in benzene-methyl alcohol mixtures. Solutions in benzene 85: methyl alcohol 15 obey van't Hoff's law at 25° C<sup>22</sup>, while the methyl alcohol content required for precipitation from 0.2 per cent solutions of a rubber fraction of molecular weight 150,000 was found to be 18.3 per cent at 25° C. The limiting form of Equation (2) for infinitely dilute solutions may conveniently be written in terms of  $v_1$  by substituting  $p \simeq \frac{lw_1}{1 - v_1}$ , to give:

$$\alpha v_1^2 - v_1\{\alpha - (\beta - \zeta) + (\gamma - \zeta/l)\} + (\gamma - \zeta/l) = 0 \quad (25)$$

If there are any critical points in the solvent power of a given mixture, they will be represented by roots of (25), such that  $0 < v_1 < 1$ . Three cases have to be considered, according as the separate liquids are solvents or not.

*Neither Liquid a Solvent.* The polymer dissolves in a single liquid (0) if  $T\Delta S_0^r > \Delta H_0$ . The condition for the two liquids to be nonsolvents are, therefore, respectively  $\beta > \zeta$ ,  $\gamma > \zeta/l$ . Under these circumstances it can be shown that (25) has two real roots between 0 and 1 if  $\alpha$  is sufficiently large compared with  $(\beta - \zeta)$  and  $(\gamma - \zeta/l)$ . In particular, if  $\beta - \zeta = \gamma - \zeta/l$ , the condition for two real and positive roots is:

$$\alpha > 4(\beta - \zeta) \quad (26)$$

Thus, if  $\alpha$  is large enough, mixtures of two nonsolvents may be solvents over a certain concentration range, the extent of this range increasing<sup>23</sup> with  $\alpha$ . In other words, the most striking feature of the solvent properties of mixed liquids finds a ready interpretation.

*Mixture of Solvent and Nonsolvent.* If liquid (1) is the solvent,  $(\beta - \zeta) < 0 < (\gamma - \zeta/l)$ , and it is easily seen that (25) must have two real roots, of which only one can lie between 0 and 1. This, of course, is only a mathematical representation of the physically obvious fact that there must be a critical mixture of a solvent and a nonsolvent, but it is to be noted that its composition depends on  $\alpha$  as well as on  $\beta$  and  $\gamma$ . The larger the value of  $\alpha$ , for given  $\zeta - \beta$  and  $\gamma - \zeta/l$ , the greater the proportion of nonsolvent in the critical mixture<sup>24</sup>. The very interesting problem of the dependence of the critical composition on the molecular weight of the polymer lies, of course, outside the scope of this treatment.

*Mixtures of Two Solvents.* Such mixtures are of less interest than the other types, but we may note the possibility predicted by Equation (25) that the mixture might be a nonsolvent over a certain range of composition. This could only happen if  $\alpha$  had a large negative value, which would imply energetic interaction between the two liquids. Since this would also involve a reduced entropy of mixing, it is evident that the present analysis could not hold quantitatively. It is of interest to note that this possibility is realized experimentally by cellulose acetate in mixtures of aniline and glacial acetic acid. Mardles<sup>25</sup> found the solvent power of mixtures to be much less than those of the components at 20° C, and at lower temperatures precipitation may be produced by adding acetic acid to an aniline solution. The origin of the interaction between the two liquids is here very obvious.

#### ESTIMATION OF THE CONSTANTS

Before the equations developed above can be used to predict the behavior of any selected three-component mixture, it is necessary to know the constants  $\alpha$ ,  $\beta$ ,  $\gamma$ , and also the function  $\Delta S_0^r$ . As explained in the previous paper,  $\Delta S_0^r$  is assumed to have the value calculated for an athermal mixture of polymer + liquid. Several expressions have been derived for this function, from which we have arbitrarily selected Miller's (Equation (2)). The value to be assigned to the coordination number  $Z$  is uncertain, but 6 has been taken as reasonable in the present application. The assumption that a single function  $\Delta S_0^r$  of such simplicity is quantitatively applicable to any mixture of polymer + liquid is quite unproved, and we shall, in fact, shortly publish some data which show it to be only approximately valid.

Equation (2) applies to linear polymers; the effect of any cross-linking which may be present is to reduce the entropy of swelling. An estimate of the amount ( $-\delta\Delta S_0^r$ ) of this reduction has recently been given by Flory and Rehner<sup>26</sup>, in the form:

$$\delta\Delta S_0^r = R \frac{\rho_r V_0}{M_c} \cdot v_r^{\frac{1}{3}} \quad (26)$$

where  $M$  is the "molecular weight" of the average section of polymer chain included between consecutive junction points of the network. Since we have no independent estimate of  $M_c$ , the equation actually used below is  $\delta\Delta S_0^r = 0.04v_r^{\frac{1}{3}}$ , the constant being chosen so as to make  $\Delta S_0^r = 0$  at a value of  $v_r$  corresponding roughly with the maximum extent of swelling of a typical vul-

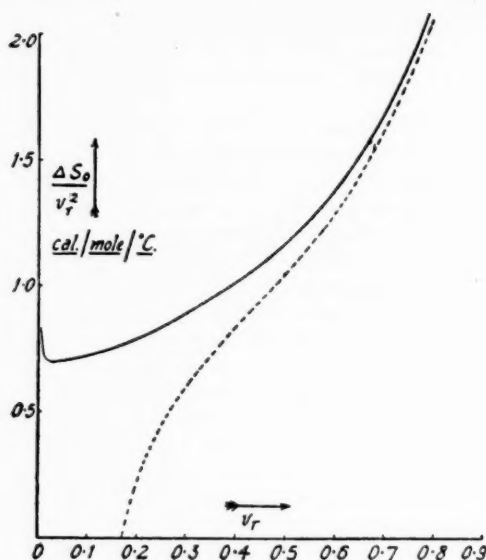


FIG. 1.—Entropy of dilution for linear (solid line) and cross-linked (dotted line) polymers.

canized rubber in a good swelling agent. Figure 1 gives plots of  $\Delta S_0^r/v_r^2$  for raw and vulcanized rubber calculated as just described; these have been used without further modification in all the quantitative applications of the next section<sup>27</sup>.

The constant  $\alpha$  is readily obtained by calorimetric measurement of the heat of mixing of the two liquids. It is an assumption of the present treatment that  $\alpha$  is independent of the liquid composition, which is well known to be true for many simple pairs of liquids<sup>28</sup>, although it fails badly for mixtures of hydrocarbons with highly associated liquids such as alcohols. The only pair of liquids used in this work for which the constancy of  $\alpha$  has been tested directly is hexane + methyl acetate, which was selected as one having a large  $\alpha$  and particularly interesting solvent properties. The heat of mixing was measured by (Miss) J. Ferry, by a method to be described elsewhere, and gave the results shown in Figure 2, where  $\alpha$  is plotted as a function of the hexane content.

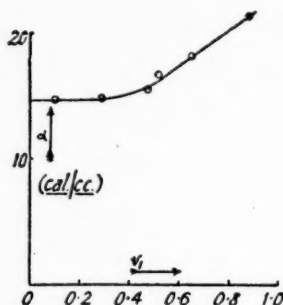


FIG. 2.—Heat of mixing of hexane (1) and methyl acetate (2).



It will be seen that  $\alpha$  is by no means accurately constant, but it is unlikely that the deviation found here is exceeded by any of the other pairs of liquids used. Values of  $\alpha$  for these were obtained by measuring the temperature change on mixing 2 cc. of each liquid in a small vacuum jacketed calorimeter; they are therefore much less precise than that for hexane-methyl acetate.

The constants  $\beta$  and  $\gamma$  could be obtained from the heats of mixing of the polymer with the separate liquids, but no reliable values of these were available for any of the systems examined. The method adopted was therefore based on measurements of the limited swelling of vulcanized rubbers in the single liquids. As an example of the procedure, consider the estimation of  $\beta$  and  $\gamma$  for the system Neoprene-GN—hexane—methyl acetate. The limiting swelling of a pure-gum vulcanizate in hexane at 25° C was 0.348 cc. per gram of rubber; in methyl acetate 0.490 cc. per gram. The density of the rubber being 1.271, the corresponding values of  $v_r$  are calculated to be 0.693, 0.617. Now the thermodynamic condition for equilibrium swelling in hexane is:

$$\frac{\Delta S_0^r}{v_r^2} = \frac{\beta V_1}{T}$$

From Figure 1,  $\Delta S_0^r/v_r^2 = 1.57$  for a vulcanized rubber at  $v_r = 0.693$ , so that, putting  $V_1 = 127$ ,  $T = 298$ , we obtain  $\beta = 3.68$ . Similarly,  $V_2 = 80$ ,  $\gamma = 4.92$ . Values of  $\beta$  and  $\gamma$  found for a vulcanized rubber are assumed to apply to the corresponding raw rubber, which will in general be a sufficiently good approximation. The method could, of course, be applied directly to raw rubbers in liquids which were not solvents.

It is important to realize that this method of obtaining  $\beta$  and  $\gamma$  will to some extent provide an automatic compensation for deficiencies of the theory. It will be shown in a forthcoming publication that the free energy of dilution of a polymer liquid mixture generally follows closely the form  $\Delta G_0 = kv_r^2 - T\Delta S_0^r$ , where  $\Delta S_0^r$  is given its theoretical value, but that  $kv_r^2$  is not in general exactly equal to  $\Delta H_0$ . In obtaining  $\beta$  and  $\gamma$  as described above, we are actually fitting each constant to a single point on the free energy curve. It does not follow that  $\beta V_1 v_r^2$  is a precise measure of the heat of dilution of the polymer by liquid 1.

#### PREDICTION OF SOLUBILITY AND SWELLING FROM COHESIVE ENERGY DENSITIES

The above methods of estimating  $\alpha$ ,  $\beta$ ,  $\gamma$  suffer from the disadvantage of requiring measurements on all three binary mixtures. While the observations required are very simple, it would clearly be a great advantage if the behavior of a ternary mixture could be predicted from properties of the single components. It has been shown<sup>29</sup> that the cohesive energy densities of liquids form a basis on which their swelling powers for a given vulcanized rubber can be arranged roughly in order. If  $e_r$  and  $e_1$  are the cohesive energy densities (calories per cc.) of rubber and liquid, the swelling is roughly a function of  $V_1(\sqrt{e_1} - \sqrt{e_r})^2$ . A similar treatment is readily extended to ternary mixtures. Writing  $e_2$  for the cohesive energy density of the second liquid, we have, using Hildebrand's expression<sup>28</sup>:

$$\left. \begin{aligned} \alpha &\approx (\sqrt{e_1} - \sqrt{e_2})^2 \\ \beta &\approx (\sqrt{e_1} - \sqrt{e_r})^2 \\ \gamma &\approx (\sqrt{e_2} - \sqrt{e_r})^2 \end{aligned} \right\} \quad (27)$$



Constants calculated in this way are generally too small, frequently by a factor of 2 or 3, but for a given polymer in a range of liquids, values of  $\beta$  usually follow  $(\sqrt{e_1} - \sqrt{e_r})^2$  quite closely, as is shown by the smoothness of a plot<sup>29</sup> of swelling as a function of  $V_1(\sqrt{e_1} - \sqrt{e_r})^2$ .

Equations (27) give a relationship between  $\alpha$ ,  $\beta$ , and  $\gamma$ :

$$\alpha \approx (\sqrt{\beta} \pm \sqrt{\gamma})^2 \quad (28)$$

This fits the data for the system Neoprene-GN—hexane—methyl acetate quite well, since  $(\sqrt{\beta} + \sqrt{\gamma})^2 = 17.1$ , which is within the range of  $\alpha$  found experimentally, but comparison with the literature shows that it is not generally accurately true for sets of three liquids.

Despite the shortcomings of Equations (27) and (28) for quantitative application, they form a basis for some very useful predictions as to the behavior of mixed liquids. The value of  $e_r$  for a given polymer may be estimated from its swelling in a range of liquids<sup>29</sup> or, approximately, from its chemical constitution. Solvents for the raw polymer, or good swelling agents for a vulcanizate, would then be sought among liquids whose cohesive energy densities were close to that of the polymer. Since the heat of mixing depends on  $(\sqrt{e_1} - \sqrt{e_r})^2$ , two liquids 1 and 2 may have similar swelling powers if  $e_1 \approx e_2$ , or if  $\sqrt{e_1} - \sqrt{e_r} \approx \sqrt{e_2} - \sqrt{e_r}$ . In the former case  $\alpha \approx 0$ ; in the latter  $\alpha \approx 4\beta$ . Now, the foregoing analysis has shown the dependence on  $\alpha$  of the solvent properties of mixture, and it is evident that the swelling or solvent power of the latter mixture is much greater than that of the former. Thus, if we wish to find a pair of nonsolvents which mix to form a solvent for a given polymer, it is necessary to select two liquids whose cohesive energy densities lie on opposite sides of that of the polymer that we wish to dissolve. All mixtures of this type examined have, in fact, shown enhanced swelling power, and a number of cases of nonsolvents mixing to produce a solvent have been discovered; some examples are given later.

The effect of polar liquids in enhancing the solvent power of paraffin hydrocarbons for natural rubber is also to be anticipated on this basis. The cohesive energy densities of the lower paraffins are less than that of rubber (63.7 calories per cc.)<sup>29</sup>, those of the effective polar liquids much higher, so that  $\beta$  is small,  $\gamma$  larger, and  $\alpha \approx (\sqrt{\beta} + \sqrt{\gamma})^2$ .

It is evident from these considerations that the treatment of mixed liquids as single ones is of very limited validity. Mixtures of liquids sufficiently similar to have  $\alpha \approx 0$  will seldom be used in practice, so the solvent power of mixtures likely to find application generally exceeds the mean of their components.

## EXPERIMENTAL TESTS OF THE THEORY

*Solubility of Rubbers in Mixed Liquids.* For an adequate test of the theory, it is desirable to be able to select solvents and nonsolvents which have cohesive energy densities lying on both sides of that of the rubber. Since this cannot be conveniently done for natural rubber, work has been carried out on Neoprene-GN, Buna-S, and Buna-N. All were lightly milled before use, so that they dissolved readily in suitable solvents<sup>30</sup>. An attempt was made first to interpret solvent behavior qualitatively in terms of cohesive energy densities, and the results are set out in Table I below. The liquids are divided into two groups according to their cohesive energy densities, working away from the value for the rubber. (S) following the name of a liquid indicates that it is a

TABLE I  
SOLUBILITY OF RUBBERS IN MIXED LIQUIDS

Rubber	$\sqrt{e}$ (calories per cc.) <sup>†</sup>	Liquid 1	$\sqrt{e_1}$ (calories per cc.) <sup>‡</sup>	Liquid 2	$\sqrt{e_2}$ (calories per cc.) <sup>‡</sup>
Neoprene-GN	8.2	Diisopropyl ketone (S)	8.1	$\longrightarrow$ <i>n</i> -Propyl acetate (S)	8.75
		Ethyl ether	7.6	$\longrightarrow$ Ethyl acetate	9.1
		Hexane *	7.4	$\longrightarrow$ Methyl acetate	9.6
		Pentane †	7.1	$\longrightarrow$ Acetone	9.8
				$\longrightarrow$ Methyl formate	10.2
Buna-S	8.1	Ethyl ether (S)	7.6		
		Hexane * (S)	7.4	$\longrightarrow$ <i>iso</i> -Butyl acetate (S)	8.3
		Pentane †	7.1	$\longrightarrow$ Ethyl acetate	9.1
				$\longrightarrow$ Methyl acetate	9.6
Buna-N	9.4			$\longrightarrow$ Acetone	9.8
		Ethyl methyl ketone (S)	9.2	$\longrightarrow$ Methyl formate (S)	10.2
		Toluene	8.9	$\longrightarrow$ Ethyl cyanoacetate	(11)
		<i>p</i> -Cymene	(8.5)	$\longrightarrow$ Dimethyl malonate	(11)

\* B. D. H. "Spectroscopic" *n*-hexane.

† A low fraction of petrol ether, boiling range 44/46°.

solvent. Two liquids joined by a full line are nonsolvents which form a solvent mixture; two liquids joined by a dotted line are nonsolvents which do not form a solvent mixture. Cohesive energy densities are in general quoted from an earlier paper<sup>29</sup>; bracketted values are estimated from chemical structure. Solubilities were determined simply by trying to disperse about 0.1 gram of rubber in 10 cc. of liquid by standing overnight at room temperature, and then shaking vigorously by hand.

The next step was to test the validity of Equation (25) in giving quantitatively the critical solubility limits for a number of mixed liquids. These limits were determined by adding nonsolvent from a burette to a 1 per cent solution of the rubber at 25° C, until a definite opalescence was observed. The end point was not very precise in some cases, and it is also to be observed that the equations were derived for rubbers of infinite molecular weight, so that one would expect the experimental solubility range to exceed slightly the theoretical one. The results are set out in Table II.

It is evident that agreement between theory and experiment is by no means quantitative. Taking the first line of the table as a rather bad example, the

TABLE II  
CRITICAL SOLUBILITY LIMITS FOR RUBBERS AT 25° C

Rubber	Liquids		$\alpha$	$\beta$	$\gamma$	$\zeta$	$l$	$\eta$	
	(1)	(2)						Calculated	Observed
Neoprene-GN	Hexane	Methyl acetate	16	3.7	4.9	1.6	0.63	0.19; 0.79	0.40; 0.64
	"	Acetone	14.8	3.7	5.8	1.6	0.58	0.25; 0.81	0.38; 0.68
	Benzene	"	1.5	1.1	5.4	2.1	0.83	0.63	0.17
	"	Methyl acetate	4.7	1.1	4.9	2.1	1.01	0.42	0.19
	"	Hexane	8.6	1.1	3.7	2.1	1.44	0.18	0.19
Buna-S	Pentane	Methyl formate	20.8	4.8	9.0	1.7	0.54	0.36; 0.77	Not solvent
	"	Ethyl acetate	10.3	2.8	3.1	1.8	0.85	0.11; 0.89	0.15; 0.85
	"	Methyl acetate	15.2	2.8	5.9	1.8	0.69	0.24; 0.91	0.35; 0.90
Buna-N	Dimethyl malonate	Toluene	7.6	3.4	2.5	1.8	0.93	0.10; 0.76	0.12; 0.57
	Ethylcyanoacetate	<i>p</i> -Cymene	7.2	2.8	3.9	1.9	1.47	0.48; 0.76	0.38; 0.63
	"	"							

observed and calculated values of  $v_1$  can be made to agree by reducing  $\alpha$  from 16 to 9.3, leaving the other constants unchanged. In this particular case at least, the discrepancy is not surprising, since determination of the densities of mixtures of hexane and methyl acetate shows that there is a very large expansion on mixing, amounting to almost 2 per cent for a 50:50 mixture. This expansion produces a considerable reduction in the cohesive energy of the mixture, and therefore an absorption of heat on mixing which is much larger than would otherwise be observed. The theoretical development of course expressly excludes any effect of volume changes.

### SWELLING OF VULCANIZED RUBBERS

A large number of determinations have been made of the maximum swelling of vulcanized rubbers in mixed liquids. The method consisted of allowing the rubber to swell in a considerable excess of liquid for 3 days and then weighing, after rapidly removing surface liquid. This method works well for simple liquids, but is not quite precise for mixtures, since the liquid imbibed does not in general have the same composition as the residue. In converting the measured weight absorption to a volume, the assumption of the density of the swelling medium therefore introduces some error, but this is not sufficient to affect the main conclusions. In the next section, details of some more precise measurements are reported. Here we select as typical three sets of measurements.

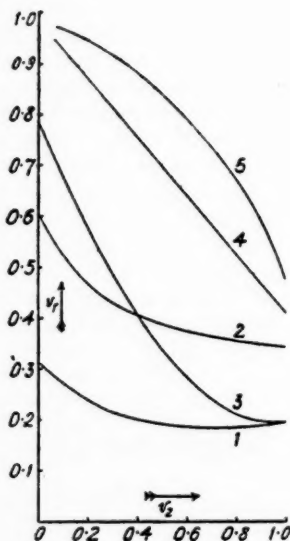


FIG. 3.—Swelling of vulcanized rubbers in pentane (1) + benzene (2). Curve 1, Natural rubber; 2, Buna-S; 3, Neoprene-GN; 4, Buna-N; 5, Thiokol-FA.

(Figure 3.) *Swelling of a Series of Rubbers in Pentane-benzene Mixtures.* The vulcanizates had the same compositions as those used in earlier work<sup>9</sup>, the natural rubber and Neoprene-GN data being for pure gum mixes (rubbers 1 and 6 of Reference 29). The estimated constants for the various systems are shown in Table III. Data are plotted as  $v_r$  for the swollen rubber against  $v_2$ ,

TABLE III

Rubber	$\alpha$	$\beta$ (calories per cc.)	$\gamma$	$l$
Natural rubber	9	1.6	0.7	0.76
Buna-S	9	3.3	2.4	0.76
Neoprene-GN	9	5.1	0.8	0.76
Buna-N	9	ca. 15	2.9	0.76
Thiokol-FA	9	" 25	3.3	0.76

the volume fraction of benzene, this being related to the maximum swelling  $Q$  (cc. of liquid per gram of rubber) by  $v_r = \frac{1/\rho_r}{Q + 1/\rho_r}$ . There is a very inter-

esting progressive change in the form of the curves as  $\beta$  becomes comparable with  $\alpha$ . Natural rubber shows a pronounced maximum swelling in 70 per cent benzene,  $\alpha$  being much larger than  $\beta$  or  $\gamma$ . Buna-S and Neoprene-GN also show enhanced swelling, though without a definite maximum, the difference between  $\alpha$  and the other constants being somewhat less. Buna-N and Thiokol-FA have large  $\beta$  values, and show normal, or even reduced, swelling in mixtures.

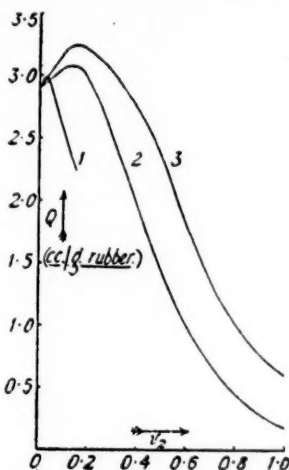


FIG. 4.—Swelling of vulcanized natural rubber in hexane (1) + polar liquid (2). Polar liquid—(1) ethyl alcohol; (2) acetone; (3) ethylmethyl ketone.

(Figure 4.) *Swelling of Natural Rubber in Mixtures of Hexane with a Highly Polar Liquid.* These mixtures are of the same type as those whose solvent powers were studied by Kemp and Peters<sup>18</sup>. In the three cases examined, a maximum was found in the swelling curve, despite the very small swelling power of the polar liquids. Constants for the ketone mixtures (below) show  $\alpha$  to be large compared with  $\beta$  and  $\gamma$ ; none are included for ethyl alcohol, owing to the great asymmetry of its heat of mixing with hydrocarbons<sup>21</sup>.

Liquid 2	$\alpha$	$\beta$ (cals. per cc.)	$\gamma$	$l$
Acetone	14.8	1.2	9.5	0.58
Ethylmethyl ketone	11.3	1.2	4.5	0.70

(Figure 5.) *Swelling of Vulcanized Buna-S in a Range of Pairs of Liquids Chosen so as to Cover a Range of Values of  $\alpha$ .*

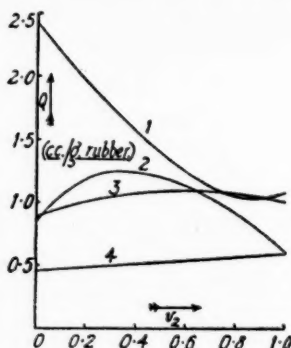


Fig. 5.—Swelling of vulcanized Buna-S in mixed liquids.

Curve	Liquid 1	Liquid 2	$\alpha$	$\beta$ (cals. per cc.)	$\gamma$	
1.	Chloroform	<i>n</i> -butyl acetate	-13	2.2	2.3	1.65
2.	Hexane	ethyl acetate	5.1	2.6	4.1	0.75
3.	Ethyl ether	<i>n</i> -propyl acetate	-0.6	3.3	2.7	1.10
4.	Ethylmethyl ketone	ethyl acetate	0.3	5.1	4.1	1.10

Curve 1 is interesting, as it represents an example of a pair of liquids which interact strongly with one another,  $\alpha$  being highly negative, and the swelling curve showing a minimum. In other words, the swelling power of *n*-butyl acetate is slightly reduced by adding a small proportion of the much more powerful swelling agent chloroform. Curve 2 gives another example of enhanced swelling associated with a large  $\alpha$ . Curves 3 and 4 show almost normal swelling, with  $\alpha$  small in both cases. The slight maximum in Curve 3 was anticipated from the cohesive energy densities ( $\sqrt{e_1} = 7.6$ ;  $\sqrt{e_r} = 8.1$ ;  $\sqrt{e_2} = 8.7$ ), but the small negative value of  $\alpha$  is unexplained, a positive value of about 3 having been expected.

Considering all the data, the theory is qualitatively successful, and this is also true of many similar figures obtained in these laboratories. Reference may be made to one rather striking case reported by Tomkins<sup>32</sup>, who showed mixtures of benzene and carbon disulfide to be even better swelling agents for natural rubber than either separately, although both are already extremely good. In this case  $\beta$  and  $\gamma$  are both small, while from the data of Gerard and Schmidt<sup>33</sup>,  $\alpha = 8$ .

#### DISTRIBUTION OF MIXED LIQUIDS BETWEEN TWO PHASES

A complete test of the ability of Equations (13) (with  $\Pi = 0$ ) to describe the swelling of a polymer in a mixture of two liquids requires the determination of the liquid ratios in both phases. Measurements of this kind have already been carried out by Brønsted and Volqvartz<sup>17</sup> for polystyrene. Unfortunately, in many of the cases they studied, one liquid (sometimes both) was a relatively long chain compound, *e.g.*, a lauric ester, which should be considered as a low polymer rather than as a liquid. The present treatment would thus not apply quantitatively, but their results are of considerable qualitative interest. The liquids used may be roughly classified according to cohesive energy density in three groups.

(1) Nonsolvents of low C.E.D.

*n*-dibutyl ether  
*n*-propyl laurate

(2) Solvents

ethyl laurate  
methyl laurate  
*n*-butyl sebacate  
dibenzyl ether  
*iso*-amyl benzoate  
benzyl benzoate  
*m*-cresol

(3) Nonsolvents of high C.E.D.

acetone  
ethyleneglycol monoacetate  
acetonitrile  
*n*-butyl alcohol  
ethyl alcohol

Mixtures of two liquids from group (1) or two from (3) show the normal swelling which we have associated with small values of  $\alpha$ , together with fairly uniform distribution of the two liquids between the two phases. Mixtures of a solvent with a nonsolvent show a considerable asymmetry in liquid distribution, the solvent being preferentially absorbed by the polymer. Only one example is given of a mixture of liquids from groups (1) and (3); here we find that acetone and *n*-propyl laurate combine to form solvent mixtures, over the composition range 12 to 63 per cent acetone. The distribution is interesting: from mixtures containing <12 per cent acetone, acetone is preferentially imbibed; from mixtures containing >63 per cent acetone, *n*-propyl acetate. In other words the distribution in the polymer phase is more uniform than that in the swelling medium. All these results are thus in qualitative agreement with our theory.

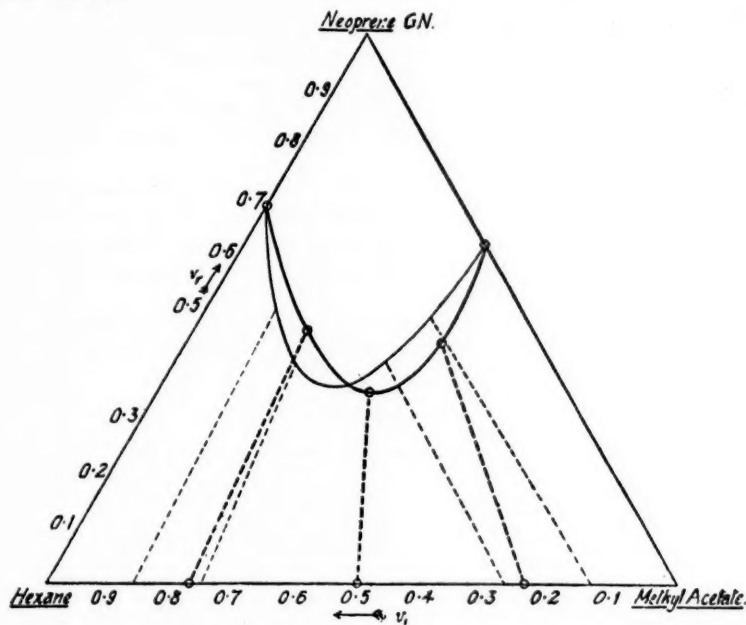


Fig. 6.—Vulcanized Neoprene-GN in hexane (1) + methyl acetate (2) at 25° C.

A complete study has been made of the behavior of the system: vulcanized Neoprene-GN-hexane-methyl acetate at 25° C. Samples of the rubber were immersed in 10 cc. of liquid of known composition, the weight of rubber being chosen so that 1 to 1.5 cc. of liquid was absorbed. After 3 days the rubber



was removed, surface-dried, weighed, and the whole of the absorbed liquid distilled off *in vacuo*. The composition of the distillate was determined from its density, using a pycnometer holding about 0.7 cc. From these measurements the complete compositions of both phases are readily obtained, although the accuracy is not very high. The results are shown by the heavy lines in Figure 6, in which the thin lines were calculated<sup>24</sup> from Equations (13) by taking  $\alpha = 9.3$ ,  $\beta = 3.68$ ,  $\gamma = 4.92$ ,  $l = 0.63$ . The value of  $\alpha$  is that required to make the theoretical and experimental solubility limits for raw Neoprene-GN agree (see section on solubility of rubbers in mixed liquids), and not the calorimetric value. The maximum swelling found experimentally agrees with calculation, but neither the distribution nor the form of the swelling curve is exact. A closer fit could undoubtedly be obtained by a quite legitimate adjustment of the curve assumed for  $\Delta S_0^r$ , but the labor involved in repeating the calculations would scarcely be justified. It is evident that we have at this point reached, or passed, the limits of useful application of the analysis which has been presented.

### SUMMARY

The equations derived in the previous paper for the osmotic equilibrium between a ternary mixture of polymer + two liquids and a mixture of the two liquids are applied to the swelling of cross-linked polymers in mixed liquids and to the solubility of linear polymers in mixed liquids.

A mixed liquid has solvent properties intermediate between those of its components only when these mix ideally. The larger the heat of mixing of the liquids, the greater is the solvent power of the mixture relative to those of the components. This conclusion forms the basis of an explanation of the enhanced swelling of rubbers in pairs of dissimilar liquids and of the fact that a mixture of two nonsolvents may be a solvent over a certain range of concentration.

Experimental results are given for the swelling of vulcanized rubbers and the critical solubility limits of unvulcanized rubbers. It is shown that these can be explained qualitatively from the cohesive energy densities of the three components, and semiquantitatively from the measured heats of mixing of the three binary mixtures.

The work described in these two papers forms a part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

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- <sup>5</sup> This is not in agreement with the model assumed in calculating the entropy, as Orr (see Reference 3) and Guggenheim (see Reference 4) have shown, but it appears to be very satisfactory in practice. This point will be more fully discussed in a further publication.
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<sup>16</sup> Palit, *J. Indian Chem. Soc.* **19**, 253 (1942).  
<sup>17</sup> Brønsted and Volqvartz, *Trans. Faraday Soc.* **36**, 619 (1940).  
<sup>18</sup> Kemp and Peters, *Ind. Eng. Chem.* **33**, 1391 (1941).  
<sup>19</sup> Mardles, *J. Soc. Chem. Ind.* **42**, 127 (1923); Kemp and Peters, *Ind. Eng. Chem.* **33**, 1391 (1941); Palit, *J. Indian Chem. Soc.* **19**, 253 (1942); Doolittle, *Ind. Eng. Chem.* **36**, 239 (1944).  
<sup>20</sup> For convenience of reference, the numbering of equations is continued from the previous paper (Part V).  
<sup>21</sup> Brønsted and Volqvartz, *Trans. Faraday Soc.* **35**, 576 (1939).  
<sup>22</sup> Gee, *Trans. Faraday Soc.* **36**, 1171 (1939).  
<sup>23</sup> The validity of this conclusion is limited by the fact that if  $\alpha$  becomes too large, the liquids themselves are not miscible in all proportions. For any value of  $\alpha$ , a critical mixing temperature  $T_c$  for the two liquids can be found by solving the equations:

$$\left( \frac{\delta \Delta G_1^*}{\delta q} \right)_T = \left( \frac{\delta^2 \Delta G_1^*}{\delta^2 q^2} \right)_T = 0$$

For the special case of  $l = 1$ , this gives simply:

$$T_c = \alpha V_1 / (2R)$$

- <sup>24</sup> This conclusion limits the accuracy with which the dilution ratio can be used as a measure of solvent power. It has been assumed that the solvent powers of a series of liquids for a polymer can be compared by determining the amounts of a given precipitant required to bring solutions of the polymer just to the precipitation point. This is approximately the case as long as one does not encounter large variations of  $\alpha$  for a given value of  $\beta$ . As will be seen below, such variations are a very real possibility, but fortunately they can be foreseen from considerations of cohesive energy density. This method of estimating solvent power can in fact be used safely only if the solvents to be compared, and the precipitant as well, all have cohesive energy densities which lie on the same side of that of the polymer.  
<sup>25</sup> Mardles, *J. Soc. Chem. Ind.* **42**, 135 (1923).  
<sup>26</sup> Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943).  
<sup>27</sup> It is of interest to note that the curve of  $\Delta S_0^*/V_r^2$  for vulcanized rubber does not differ very significantly from that suggested empirically by the author in an earlier discussion (*Trans. Faraday Soc.* **38**, 418 (1942)).  
<sup>28</sup> Hildebrand, "Solubility", Reinhold Publishing Corp., New York, 1936.  
<sup>29</sup> Gee, *Trans. Inst. Rubber Ind.* **18**, 266 (1943).  
<sup>30</sup> As received, all are difficult to disperse in any solvent, due presumably to a small amount of cross-linking.  
<sup>31</sup> Wolf, Pahlke and Wehage, *Z. physik. Chem.* **28**, 1 (1935).  
<sup>32</sup> Tompkins, *Trans. Faraday Soc.* **16**, Appendix, p. 162 (1921).  
<sup>33</sup> Gerard and Schmidt, *Z. physik. Chem.* **121**, 221 (1926).  
<sup>34</sup> The method of solution was to write Equations (13) as  $\left\{ \begin{array}{l} F_1(q) = f_1(p, V_r) \\ F_2(q) = f_2(p, V_r) \end{array} \right\}$ , prepare graphs of  $F_1$  and  $F_2$ , and then to solve each equation separately for a series of values of  $V_r$ , so as to obtain solutions  $q_1 q_2$  for each trial value of  $p$ . The required solution is that value of  $p$  which makes  $q_1 = q_2$ , and was found by graphical interpolation.

# THE MELTING OF CRYSTALLINE POLYMERS \*

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Early theories of the liquid state were based on analogies with imperfect gases. Recently the application of x-ray methods has shown liquids to have a pseudo-crystalline structure. Theories based on a similarity between the liquid and crystalline states have consequently been developed and are, naturally, most successful in predicting properties near the melting point. Such theories have recently been discussed critically by Mott and Gurney<sup>1</sup>. In this connection the concept of the degree of order of a system has proved to be of considerable value, and has been applied to critical phenomena by a number of authors, notably Lennard-Jones and Devonshire<sup>2</sup>. Phase transitions have been treated as order-disorder transformations, and melting is characterized by an abrupt change in the degree of order of the system as the temperature is raised.

All such theories predict a sharp melting-point of low-molecular compounds in agreement with experiment. If, however, we study the melting-point of long-chain polymers, two phenomena seem to require further explanation. The convergence of the melting points of a homologous series was considered by Eyring<sup>3</sup> to be evidence for the segmental theory of polymers, but we shall show here that this convergence follows naturally from the thermodynamic properties of the system. Here our argument is rather similar to that of Mark<sup>4</sup>, who showed that if the heat and entropy of fusion were both almost linear in the number of links in a chain, a convergent melting temperature automatically followed. The second and more fundamental feature in the melting of polymers is the existence of a range of melting, and the coexistence over a range of temperature of crystalline and amorphous material in equilibrium. Such a range has been known for some time to exist in rubber, but it is only recently that quantitative data have become available. A melting range also exists in polyethylene, and it would seem to be a general property of crystalline high polymers. It is possible that these phenomena are connected with the premelting properties of long-chain paraffins and ketones which have been extensively studied by Muller, Ubbelohde and Oldham<sup>5</sup>. Frenkel<sup>6</sup> has discussed premelting in terms of his theory of heterophase fluctuations, which has certain formal similarities with the views we develop below.

## CRYSTALLIZATION OF UNSTRETCHED POLYMERS

We have, initially, two objects. First, to calculate the melting point of a crystalline polymer in terms of fundamental molecular magnitudes, and thus show how the melting temperature converges to a fixed value as the chain length becomes large. Secondly, we have to explain the absence of a sharp melting point and to derive an expression for the crystalline-amorphous ratio

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at various temperatures. To do this we set up the Gibbs free energy  $G$  of a system in which a fraction  $\theta$  of material is amorphous, the remainder being crystalline.

The parameter  $\theta$  may be introduced in two ways:

1. Each chain is regarded as being completely crystalline or completely amorphous. Thus out of  $N$  total chains,  $\theta N$  form a distinct amorphous,  $(1 - \theta)N$  a distinct crystalline phase.

2. We may imagine each chain to be composite, containing a fraction  $\theta$  of amorphous links and  $(1 - \theta)$  crystalline ones. There are  $N$  such chains, but only a single composite phase.

The equilibrium condition  $dG = 0$  has to be formulated in different ways in the two cases.

We take as our ultimate model an assembly of chains in which amorphous regions of chain segments separate regions of ordered crystalline structure. A given chain will pass through several of these regions: our model thus corresponds to the case 2 above, and is shown diagrammatically in Figure 1. The

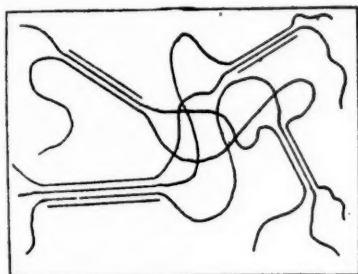


Fig. 1.—Mixed or composite phase model.

evidence for this "fringed micelle" theory of the partially crystalline mass comes chiefly from x-rays, and has been discussed in more detail elsewhere<sup>7</sup>. We assume that in a completely amorphous structure there exist entanglements which act as nuclei for crystal growth; this occurs out along the chains comprising the entanglement.

The equilibrium condition  $dG = 0$  at the melting point corresponds to  $T = T_m = \Delta H / \Delta S$ , where  $\Delta H$  and  $\Delta S$  are the heat and entropy of fusion of the system. For the model corresponding to Figure 1 (case 2 above), we show that  $T_m$  is a function of  $\theta$ , and that this arises from a nonlinear dependence of  $G$  on  $\theta$  defined as in 2. This point has already been noted by Alfrey and Mark<sup>8</sup>, and considered qualitatively in terms of a model which is a simplified form of Figure 1. They discuss the behavior of a single chain containing crystalline and amorphous regions joined in series. As crystallization proceeds, both  $L$ , the distance between the ends of an amorphous segment, and  $n$ , the number of links in it, decrease. If  $L$  is given in terms of a Kuhn probability factor, it can be seen that  $L$  decreases more rapidly than  $n$ . This means that while the heat of fusion ( $\Delta H$ ) is a linear function of  $n$ , the entropy of fusion is not, and this produces a nonlinear Gibbs free energy change and a range of melting.

Here we discuss the problem from a slightly different viewpoint, but the emphasis throughout is on the nonlinear dependence of  $G$  on  $\theta$ . To make this point clear, and to illustrate the general method, we first consider a "two

phase" model, based on case 1 above, which we show gives a linear relationship between  $G$  and  $\theta$ . The melting point in this case is independent of  $\theta$  and therefore sharp. We then consider modifications based on the model of Figure 1 (case 2), which is more nearly equivalent to the physical picture of the semi-crystalline structure; we show, in this case, how  $T_m$  depends on  $\theta$ .

#### TWO-PHASE MODEL

Suppose that a single chain can exist only in a wholly crystalline or in a wholly amorphous condition. Consider an assembly of  $N$  chains of which  $N_A$  are completely amorphous and  $N_K$  completely crystalline. Suppose further that each chain consists of  $p$  links: these links are statistical elements which may not coincide with the monomeric unit of the polymer; in general, however, a link will be a small multiple of this unit.

If, then,  $\theta$  is the proportion of amorphous material in the structure, and  $(1 - \theta)$  the corresponding amount of crystalline material,  $\theta$  is defined by:

$$\theta = \frac{N_A}{N_A + N_K} = \frac{N_A}{N} \quad \text{and} \quad 1 - \theta = \frac{N_K}{N_A + N_K} = \frac{N_K}{N} \quad (1)$$

If we imagine the amorphous part of the structure to be built up on a lattice frame-work of coördination number  $Z$ , we can write the statistical weight factor  $\Omega$  of the  $N_A$  amorphous chains as:

$$\log \Omega = \log \left[ \left( \frac{Z-1}{e} \right)^{p-1} \frac{p}{\sigma} \right]^{N_A} = \log (w)^{N_A} \quad (2)$$

while the statistical weight factor of the crystalline chains is 1. The number of distinct ways in which  $N_A$  chains can be arranged on the lattice  $\Omega$  is given here in the form calculated by Flory<sup>9</sup> and Huggins<sup>10</sup>;  $\sigma$  is the symmetry number of the chains.

We can now write the Gibbs free energy  $G$  of the system in terms of the appropriate partition functions as:

$$G = - N_A \chi_0^A + 3 N_A p k T \log \frac{h \nu_A}{k T} - N_A k T \log \gamma_A(T) + N_A P V_A \left. \begin{array}{l} - N_A k T \log w \end{array} \right\} \quad (3)$$

$$- N_K \chi_0^K + 3 N_K p k T \log \frac{h \nu_K}{k T} - N_K k T \log \gamma_K(T) + N_K P V_K$$

where  $\chi_0^A$  and  $\chi_0^K$  are the potential energies of a single amorphous and crystalline chain, respectively,  $\nu_A$  and  $\nu_K$  are the fundamental vibration frequencies of a link in the two phases, and  $\gamma_A(T)$ ,  $\gamma_K(T)$  the contribution to the total partition function from rotational and translational energy levels. We assume here that each chain has  $3p$  degrees of freedom and that the vibrations can be treated as perfect Planck oscillators, *i.e.*, we assume an Einstein model for each phase. The equilibrium condition for the assembly is given by:

$$dG = 0,$$

or

$$\frac{\partial G}{\partial N_A} dN_A + \frac{\partial G}{\partial N_K} dN_K = 0$$

or, since

$$dN_A = -dN_K \quad (4)$$

$$\frac{\partial G}{\partial N_A} = \frac{\partial G}{\partial N_K}$$

where  $\frac{\partial G}{\partial N_A}$  and  $\frac{\partial G}{\partial N_K}$  are the usual partial potentials ( $\mu_A$  and  $\mu_K$ ) of the chain molecules. These standard equations are to be contrasted with (7) and (8) of the next section.

Now near the melting point we may consider to a first approximation that  $v_A = v_K$ , and further that the contributions from the rotational and translational energies are equal. Thus differentiating (3) as required by (4) we get, writing now  $T = T_m$  the melting temperature:

$$\frac{\chi_0^K - \chi_0^A}{kT_m} - \frac{PV_K - PV_A}{kT_m} = (p-1) \log \frac{Z-1}{e} + \log \frac{p}{\sigma}$$

The left-hand side of this expression is  $\Lambda'/kT_m$  where  $\Lambda'$  is the latent heat of fusion at constant pressure of a single chain. It has been shown experimentally in the case of paraffins that  $\Lambda'$  is a constant multiple of the chain length  $p$ . Thus if  $\Lambda$  is the latent heat of fusion of a single link in gram molecular units, the melting-point  $T_m$  is given by:

$$\frac{p\Lambda}{RT_m} = (p-1) \log \frac{Z-1}{e} + \log \frac{p}{\sigma} \quad (5)$$

This method of determining  $T_m$  is exactly equivalent to the elementary theory of melting given by Fowler and Guggenheim<sup>11</sup>. For a simple crystal, the term  $\log \Omega$  is replaced by the entropy of disorder of the liquid  $R/\text{mole}$ , so the ratio  $\frac{\Lambda}{RT}$  should be exactly equal to 1. This has been found to be true with a fair degree of accuracy in the case of liquid metals.

Since  $T_m$  is independent of  $\theta$  in Equation (5), it follows that this model gives an abrupt change of phase. For all  $T < T_m$  the structure is completely crystalline: for all  $T > T_m$  it is completely amorphous. This follows at once from the fact that  $G$ , as defined in (3), is linear in  $N_A$  and  $N_K$ , and hence in  $\theta$ . We may write (3) in the form:

$$G = \theta G_A + (1-\theta) G_K \quad (6)$$

where  $\theta$  is defined as in (1) and  $G_A$  and  $G_K$  are the Gibbs free energies for totally amorphous and totally crystalline phases, respectively. Since  $G$  is a linear function of  $\theta$ , the position of minimum free energy which defines the melting point must be either at  $\theta = 0$  or  $\theta = 1$  according as  $G_A > G_K$  or  $G_A < G_K$ . Thus the stable form at any temperature is either completely crystalline or completely amorphous.

Any theory of this type which gives  $G$  as a linear function of  $\theta$  must always give a sharp melting point. We know from experience that crystalline and amorphous regions coexist in polymers in apparent thermodynamic equilibrium over a range of temperatures. Hence any such simple model as this will always give the wrong answer until we make  $G$  a nonlinear function of  $\theta$ . The dominant term on the right-hand side of Equation (5) is  $(p-1) \log \frac{Z-1}{e}$ .



We shall see that a similar term persists when we use a more plausible model. The term  $\log p/\sigma$  is an integrated factor imposed by oversimplification of the model. We shall see in the next section that this is replaced by a term involving  $\theta$ .

The method of applying an equation of the type (5) will be considered later. We may note briefly that since  $(p-1) \log \frac{Z-1}{e}$  is dominant and  $p$  is large, the melting point of a polyhomologous series will converge, as  $p$  increases, to a limiting  $T_m$  value given by:

$$\frac{\Delta}{RT_m} = \log \frac{Z-1}{e} \quad (6a)$$

#### COMPOSITE PHASE MODEL

We now consider the equilibrium conditions applicable to the model of Figure 1.

Suppose that the temperature is high so that the structure is completely amorphous. The statistical weight factor  $\Omega$  of the assembly of  $N$  chains each of  $p$  links is given by (2) of the last section:

$$\log \Omega = \log \left[ \left( \frac{Z-1}{e} \right)^{p-1} \frac{p}{\sigma} \right]^N$$

This expression for  $\log \Omega$  is not linear in the chain length  $p$ . The length of the molecular chains makes possible certain types of entanglement, we suppose that these entanglements have a statistical permanency. Further, we imagine that they act as nuclei for crystallization when the appropriate physical conditions favor a change from the amorphous state. Growth of these crystallites continues along the amorphous regions of the chains, until stopped by steric effects; this implies that 100 per cent crystallization can never occur, in agreement with experience.

Consider the  $N'$  amorphous segments in between two such nuclei. If the temperature is lowered sufficiently, crystallization starts so that the average number of links in a single segment is reduced from its original value  $n$ , say, to  $\theta n$  where  $\theta$  is again a factor which represents the proportion of amorphous material in the structure;  $\theta$  is now defined in terms of chain links. If the original  $n$  links in a single segment are in equilibrium when  $n_A$  of them are amorphous and  $n_K$  crystalline, the amount of amorphous material in the structure is defined as:

$$\theta = \frac{n_A}{n_A + n_K} \quad \text{and} \quad 1 - \theta = \frac{n_K}{n_A + n_K} \quad (7)$$

Provided the amorphous segments are sufficiently long, the chains in it can be considered to be nearly randomly entangled. Near the crystal nuclei the amorphous chains will be considerably restricted, but the middle portions of the chain will be free to take up all possible configurations as the restrictive factor becomes increasingly small as we go out from the nuclei. We can, therefore, write the weight factor of the  $N'$  segments as:

$$\Omega' = \left[ \left( \frac{Z-1}{e} \right)^{\theta n - 1} \frac{\theta n}{\sigma} \right]^{N'}$$

provided  $\theta n$  remains sufficiently large. We estimate that this expression is descriptive of the amorphous segments, while there is still 50 per cent or more

amorphous material in the structure. Since in effect we count as crystalline all these parts of the structure which are not completely randomly orientated, it is obvious that the  $\theta$  value we use is, in reality, too small.

We can now write the Gibbs free energy of the  $N'$  chain segments as:

$$G = -N'\theta n x_0^\Lambda + 3N'\theta n kT \log \frac{h\nu_\Lambda}{kT} - N'\theta n kT \log j_\Lambda(T) + N'P\theta n v_\Lambda \left\{ \begin{array}{l} - N'kT \log \left[ \left( \frac{Z-1}{e} \right)^{\theta n-1} \frac{\theta n}{\sigma} \right] \\ - N'(1-\theta) n x_0^K + 3N'(1-\theta) n kT \log \frac{h\nu_K}{kT} - N'(1-\theta) n kT \log j_K(T) \\ + N'P(1-\theta) n v_K \end{array} \right\} \quad (8)$$

This expression is exactly equivalent to (3), since we can write for a chain of  $p$  links, whether amorphous or crystalline  $\chi_0 = px_0$  and  $V = pv$ , where  $x_0$  and  $v$  refer to the potential energy and volume, respectively, of a single link. Further, if  $\gamma(T)$  is the rotational partition function of a chain, we put  $\gamma(T) = [j(T)]^p$ , where  $j(T)$  is the corresponding partition function of a link.

The equilibrium condition is  $dG = 0$  as before, but in this case the variable parameter  $\theta$  refers to the number of chain links.  $N'$  the number of chain segments considered remains constant throughout. Thus the equilibrium condition becomes:

$$\frac{\partial G}{\partial n_\Lambda} dn_\Lambda + \frac{\partial G}{\partial n_K} dn_K = 0$$

where  $n_\Lambda = \theta n$  and  $n_K = (1-\theta)n$  and  $\theta$  is now defined by (7). Finally, then, since  $n_\Lambda + n_K = \text{const.}$ :

$$\frac{\partial G}{\partial n_\Lambda} = \frac{\partial G}{\partial n_K} \quad (9)$$

$\partial G/\partial n_\Lambda$  and  $\partial G/\partial n_K$  are modified partial potentials corresponding to the  $\partial G/\partial N_\Lambda$  and  $\partial G/\partial N_K$  of our previous model (cf. Equation (4)).

Applying this condition to the free energy  $G$  given in (8), using the same approximations made in the last section, we get:

$$\frac{\Lambda}{RT_m} = \frac{\partial}{\partial \theta n} \left[ (\theta n - 1) \log \frac{Z-1}{e} + \log \frac{\theta n}{\sigma} \right]$$

or

$$\frac{n\Lambda}{RT_m} = n \log \frac{Z-1}{e} + \frac{1}{\theta} \quad (10)$$

where  $\Lambda$ , as before, is the latent heat of fusion of a single link. This should be contrasted with Equation (5) of the previous section.  $p$  is replaced by  $n$ , the number of links between crystal nuclei, but this is of small moment if we consider only the convergence temperature of a series, given, as before, by

$$\frac{\Lambda}{RT_m} = \log \frac{Z-1}{e}.$$

Equation (10) allows us to calculate the range of melting of a long-chain polymer in terms of various parameters; or, alternatively, to calculate the relative proportions of amorphous and crystalline material in the structure over a range of temperature. Results and methods of applying the formula are given in the next section.

## APPLICATION TO EXPERIMENTAL DATA

In deriving Equation (10) we assumed that the amorphous regions in the structure are completely random. We ignored the restrictions which the small crystallites are bound to impose on the neighboring amorphous links. This means, in effect, that we count as crystalline those parts of the amorphous segments near the crystal nuclei and our calculated value of  $\theta$  is too small. Thus, as we cool the amorphous polymer, crystallization sets in less sharply than Equation (10) would indicate. Above 50 per cent or so, crystallization these effects become increasingly dominant. In particular 100 per cent crystallization is never obtained, although allowed for by Equation (10). For rubber, Field<sup>12</sup> found a persistence of 10–20 per cent of amorphous material.

The model we use implies that  $n$  is the number of links between crystal nuclei or junction points: this means that we cannot use values for the molecular weight given by osmotic or viscosity data as in solution the whole chain length  $p$  is the determining factor. In effect we have to treat  $n$  as a parameter whose value we can only know approximately. In this connection the work of Wall<sup>13</sup> is a useful guide; in his treatment of molecular networks he obtains a molecular weight which is that of a "molecule" existing between entanglements. We use his calculated value  $n \approx 700$  for rubber.

The formula is, however, extremely sensitive to  $Z$ , the average coordination number; since  $Z$  is an average taken over a liquid structure it is not necessary to assume that it is an integer. We know suitable integral values of  $Z$  from other connections, but never accurately enough for this purpose. Thus in Equation (9) we have one experimental parameter  $\Lambda$  and two molecular parameters  $Z$  and  $n$ . Over a suitable range of  $n$  (200–700) the formula is relatively insensitive to chain length, but we have to fit a carefully chosen  $Z$  value to give  $T_m$  of the right magnitude when  $\theta = 1$  say; we then use the more accurate formula to calculate the crystalline-amorphous equilibrium over a range of temperature. In effect we need to know at least an approximate melting point before we can apply Equation (10). To illustrate this choice of  $Z$  we give two examples:

1. *Rubber*. A suitable coordination number is  $Z \approx 5.4$ . The melting point is known to be about 10° C. Taking  $n = 700$  and  $\theta = 1$ , we calculate  $T_m$  for various  $Z$  values. The results are given in Table I(a), using the value of

TABLE I

$Z$	$T_m$ °C
(a) <i>Rubber</i>	
5.0	81.5
5.3	25.3
5.4	12.3
5.5	– 1.3
6.0	–48.0
(b) <i>Paraffins and Polythenes</i>	
6	231.9
7	115.8
8	52.5

Bekkedahl and Matheson<sup>15</sup>,  $\Lambda = 4.0$  cal. per g. (272 cal. per isoprene unit)<sup>16</sup>. Thus,  $Z = 5.4$  is the most suitable coordination number for rubber. Using these figures, we calculate the value of the melting range of rubber. Using Bekkedahl's  $\Lambda$  value as before and  $Z = 5.4$ ,  $\theta = 1$  gives  $T_m = 12.3^\circ \text{C}$ ;  $\theta = 0.1$ , the lowest possible limit of amorphous material, gives  $T_m = 4.8^\circ \text{C}$ . This

range of 7–8° C is in good agreement with the experimental values of Bekkedahl and Matheson<sup>15</sup>.

2. *Paraffins and Polythenes.*—The relevant  $Z$  values here are about 6–8. For higher  $Z$  values the formula is not quite so sensitive. We give (Table I(b)) the convergent  $T_m$  values calculated from Equation (6a) for integral values of  $Z$ . Eyring<sup>3</sup> gives the convergent temperature as 122° C, and various workers have estimated it as 103–130° C. Thus  $Z = 7$  is the most suitable choice (actually  $Z = 7.0$ ).

Figure 2 shows the calculated curve for  $\theta$  plotted against temperature for polythene. Here we assume values  $n = 200$ ,  $Z = 7.0$ . The  $\Lambda$  value is given

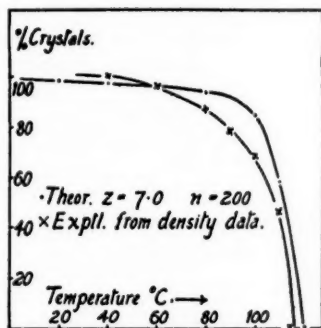


Fig. 2.—Percentage crystallinity in polyethylene as a function of temperature (mixed phase model).

by King and Garner<sup>17</sup> as 610 cal. per  $\text{CH}_2$  group. For comparison we show also a curve showing the temperature variation of the amorphous crystalline ratio calculated from experimental data<sup>18</sup> on polythene densities<sup>19</sup>. The range of temperature over which crystalline and amorphous polythenes actually co-exist is wider than the corresponding range given in Equation (10), but the deviations are in the expected direction, and the general agreement is good<sup>20</sup>.

#### APPLICATION TO PARAFFINS OF MEDIUM CHAIN LENGTH

While we should not expect the model of Figure 1 to be applicable to polymers of mediumly low chain length ( $p < 100$ ), we might expect the two phase model to be accurate in predicting melting points. x-Ray diagrams of long-chain paraffins give long spacings corresponding to nearly complete orientation of the molecules.

However, the two-phase model, for a fixed  $Z$  value, gives  $T_m$  values which converge far too flatly in the region  $p = 20$ –50. Also the  $p$ - $T_m$  curve has a minimum at a critical  $p$  value which disagrees with the smooth curve obtained experimentally. To make Equation (5) fit the experimental points for  $p < 30$ , we need to use a continually increasing  $Z$  value. If, however, we write the formula for the composite phase model with  $\theta = 1$  as:

$$\frac{\Lambda}{RT_m} = \ln. \frac{Z - 1}{e} + \frac{1}{p} \quad (11)$$

or

$$\frac{1}{T_m} = a + \frac{b}{p} \quad (11a)$$

and replace  $n$ , the number of links between nuclei by  $p$ , the total numbers of links in a chain, we might equally expect to get a formula which would fit the shorter chain molecules. Equation (11a) has been used empirically by Huggins<sup>17</sup> to describe the melting point of paraffins. For  $Z = 7$  Equation (11) gives surprisingly good agreement with the experimental  $T_m$  values over the whole range  $p < 100$ . This is shown in Figure 3 with the corresponding curves

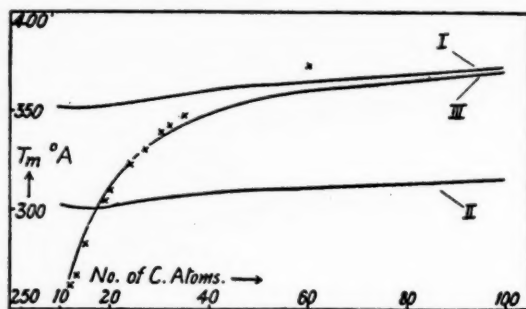


Fig. 3.—Melting points of paraffins as a function of chain length. X Experimental. I. Two-phase model  $Z = 7$ . II. Two-phase model  $Z = 8$ . III. Composite phase model  $Z = 7$ .

for the two-phase model calculated for the two coordination numbers 7 and 8.

We must note, however, that the agreement obtained is hardly covered by the arguments outlined above, and must still be regarded as something of a coincidence.

#### CRYSTALLIZATION OF STRETCHED POLYMERS

It is well known that the melting point of rubber crystals is raised by stretching: unvulcanized rubber can be crystallized at room temperature by extending to 200–300 per cent. We can give a semiquantitative explanation of the facts by a crude extension of the previous theory. Wall<sup>11</sup> gives the Gibbs free energy change on stretching  $N$  amorphous chains to a relative extent  $\alpha$  ( $\alpha = l/l_0$ : the ratio of the extended to the original macroscopic length) as:

$$\Delta G = \Delta F = \frac{1}{2} N k T (\alpha^2 + 2/\alpha - 3) \quad (12)$$

assuming no volume or internal energy change on stretching. We can apply this result immediately to the two-phase model if we assume that only the  $N_A$  amorphous chains are stretched. The equilibrium condition becomes  $\partial G / \partial \theta = 0$ , at constant  $T$ ,  $V$  and  $\alpha$ ; proceeding as before, we obtain finally:

$$\frac{p\Lambda}{RT_m} = (p - 1) \log \frac{Z - 1}{e} + \log \frac{p}{\sigma} - \frac{1}{2} (\alpha^2 + 2/\alpha - 3) \quad (13)$$

This gives the necessary increase in  $T_m$  with extension, and, as before, a sharp melting point. It is found experimentally, however, that the change from amorphous to crystalline polymeric form occurs, at a given temperature, over a range of extensions and not sharply at a particular  $\alpha$  value.

A similar simple treatment is not possible with the composite phase model, as we have not yet succeeded in relating the extension of the amorphous portion of a composite chain with  $\alpha$ , the macroscopic extension. However, by analogy with the two-phase model, we would expect this model to give an

expression of the form:

$$\frac{n\Lambda}{RT_m} = n \log \frac{Z-1}{e} + \frac{1}{\theta} - F(\alpha) \quad (14)$$

where  $F(\alpha) = 0$  when  $\alpha = 1$ . In the absence of a precise expression for  $F(\alpha)$  we assume, as a crude approximation, that we can apply the same correcting term for extension in the two cases. Then Equation (14) becomes:

$$\frac{n\Lambda}{RT_m} = n \log \frac{Z-1}{e} + \frac{1}{\theta} - \frac{1}{2}(\alpha^2 + 2/\alpha - 3) \quad (15)$$

As Equation (15) is obtained by mixing the two models, its use cannot be justified by formal thermodynamic reasoning, but the agreement with experimental data which is obtained shows that it is a useful approximation. Figure 4 shows a comparison of results from Equation (15) with the experi-

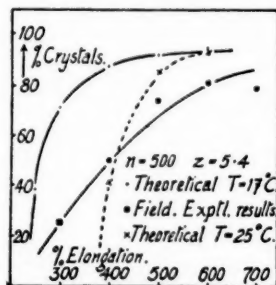


Fig. 4.—Crystallinity of rubber as a function of elongation.

TABLE II

$T$ ( $^{\circ}\text{C}$ )	Critical elongation (%)
15	175
17	250
25	400
40	600

mental data of Field<sup>10</sup> for stretched rubber. We plot the percentage of crystalline material for various elongations at a temperature of  $17^{\circ}\text{C}$ . We take  $n = 500$  and use our former value  $Z = 5.4$ . The curve rises far too sharply but the agreement is as good as can be expected.

The formula shows the extreme sensitiveness to temperature of the critical elongation at which crystallization sets in. In Table II we give approximate values for various temperatures.

These figures are quite in agreement with experience.

#### SUMMARY

The thermodynamic equilibrium which exists between crystalline and amorphous polymeric phases is discussed in terms of a fringed micelle model, as indicated by x-ray data. An expression derived for the melting point of a crystalline polymer is found to depend on the proportion  $\theta$  of amorphous material in the structure: this unsharp melting point depends ultimately on a nonlinear relationship between  $\theta$  and the free energy of the system. Calculated values of the crystalline amorphous equilibrium ratio over a range of temperature are in good agreement with experimental data. An attempt has been made to extend the calculations to the case of stretched polymers and a qualitative agreement has been found.

This work has been carried out in the Department of Colloid Science, Cambridge, and we should like to thank Professor E. K. Rideal for much



stimulating criticism. This paper arose out of discussions with Professor Sir R. H. Fowler: his advice and encouragement during its development have been invaluable to us, and we should like to record here our grateful thanks to him.

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- <sup>16</sup> We have used here Bekkedahl and Matheson's value for  $\Lambda$ , although Parks (*J. Chem. Physics* **4**, 459 (1936)) has suggested that this value is too low by a factor of 4-5. For  $T_m = 10^\circ \text{C}$ , however, Parks' tentative value gives  $Z = 24$ , which is impossibly high. More reasonable values are found if we assume that the lattice link is smaller than the isoprene unit, a view which is not improbable. Alternatively, Parks' value may be too high, and the low value of  $T_m$  for rubber compared with polyethylene might support this. In the absence of more reliable data, we have retained the original values in this and in the final section, as this will not affect the form of the relations deduced.
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- <sup>19</sup> We should like to thank J. C. Swallow of I.C.I. (Plastics), Ltd., for making available to us the exact numerical data on this point.
- <sup>20</sup> We have assumed here that the material is 100 per cent crystalline at room temperature. Since writing this paper, we have learned that 75 per cent is more nearly correct, but we have not altered Figure 2 accordingly. The point is being discussed in forthcoming papers. We are indebted to E. A. Richards for information on this point.

## THE POLYMERIZATION OF METHACRYLONITRILE. POLYMETHACRYLONITRILE.\*

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### PREPARATION OF MONOMERIC METHACRYLONITRILE

As the starting point for the preparation of methacrylonitrile, acetonecyanohydrin ( $\alpha$ -hydroxybutyronitrile) was chosen because of its ready availability<sup>1</sup>.  $\beta$ -Hydroxybutyronitrile should likewise be well suited for the purpose, but, because of the difficulties involved in its preparation, it was not utilized in the work. The removal of water can be accomplished in various ways.

(1) Phosphorus pentoxide does not give such smooth results as it does with ethylenecyanohydrin, but the reaction can be carried out successfully by centrifuging and the addition of quinoline<sup>2</sup>. Under the same conditions acetaldehydecyanohydrine (lactonitrile) yields no acrylonitrile.

(2) The thermal decomposition of acylated hydroxy-acid derivatives can be applied to acetonecyanohydrin<sup>3</sup>, but this method of preparation is difficult to carry out on a laboratory scale.

(3) Removal of water can be carried out very smoothly with thionyl chloride<sup>4</sup>. In addition to methacrylonitrile,  $\alpha$ -chloroisobutyronitrile is formed, and from the latter more methacrylonitrile can be obtained by scission of hydrogen chloride<sup>5</sup>. In this procedure, it is highly important to use pure raw materials, especially thionyl chloride, for with pure compounds the yields are higher. It is likewise advantageous to use a slight excess of thionyl chloride.

A mixture of 85 grams (1 molecular equivalent) of acetonecyanohydrin and 131 grams (1.1 molecular equivalents) of thionyl chloride are refluxed at 90°–100° C, with exclusion of all moisture. Higher temperatures give poorer yields. After 2–3 hours, evolution of hydrogen chloride and sulfur dioxide ceases, and the reaction reaches completion. By distillation 43 grams (64 per cent) of crude product is obtained. The final yield of pure methacrylonitrile is about 50 per cent; that of  $\alpha$ -chloroisobutyronitrile about 25 per cent.

A higher yield is obtained by the addition of pyridine, *e.g.*, by adding 1 molecular equivalent of pyridine per molecular equivalent of thionyl chloride, the yield of crude methacrylonitrile is increased to 73 per cent.

(4) Neither acetonecyanohydrin nor acetaldehydecyanohydrin can be transformed by silicon tetrachloride into esters of orthosilicic acid, and the latter be decomposed thermally<sup>6</sup>, even by the addition of reagents which combine with hydrogen chloride.

The methacrylonitrile used in the experiments was prepared both with phosphorus pentoxide and with thionyl chloride as reagents. It was absolutely free of halogens, and its boiling point was 88–89° C (uncorrected).

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Journal für praktische Chemie*, Vol. 160, Nos. 10–12, pages 296–314, Aug. 3, 1942. This paper, representing the Thesis of H. Fernow, Freiburg i.Br., 1940, is the 303rd Communication on Macromolecular Compounds. The preceding paper, entitled "The Polymerization of Acrylonitrile. Polyacrylonitrile", has already been published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 17, No. 2, pages 356–365, April 1944.

Analysis gave the following results:

$C_4H_5N$	Calculated	C 71.64	H 7.46	N 20.90
	Found	71.44	7.39	21.04

#### THERMAL AND CATALYTIC POLYMERIZATION OF METHACRYLONITRILE. POLYMERIZATION IN SOLUTION

Like acrylonitrile, pure methacrylonitrile does not polymerize spontaneously when heated. At temperatures up to 100° C there is no change in the monomer even after weeks of heating; above 100° C decomposition becomes noticeable.

With catalysts, in particular benzoyl peroxide, polymerization proceeds very slowly below 30° C, as in the case of acrylonitrile. A temperature range of 60–65° C was found to be particularly favorable for polymerization, in agreement with the work of Mertens and Fonteyn<sup>7</sup>.

Since polymethacrylonitrile is soluble in monomeric methacrylonitrile, whereas polyacrylonitrile is insoluble in monomeric acrylonitrile, the polymerization of methacrylonitrile obviously proceeds differently from that of the polymerization of acrylonitrile.

In the polymerization of methacrylonitrile, the polymethacrylonitrile which is formed does not precipitate, but remains in solution. Surprisingly, however, it was observed that two layers are often formed, which consist of monomeric methacrylonitrile and a solution of the polymer in the monomeric methacrylonitrile. This latter solution becomes gradually more viscous, and within a few days it solidifies to a transparent, light yellow mass. In contrast to the behavior of acrylonitrile, this polymerized mass contains no monomer after a sufficiently long time of polymerization. The product is very tough, and can be pulverized only with difficulty. All polymers prepared from pure methacrylonitrile were found to be soluble in various solvents<sup>8</sup>, including, for example, cyclohexanone, acetone, benzonitrile, methylene chloride, and methacrylonitrile.

However, by mass polymerization insoluble products with limited tendency to swell were obtained, although only from incompletely purified methacrylonitrile, and after the samples had stood at room temperature without addition of any catalyst. The products were colorless, glassy, very tough, and insoluble, and showed only a limited tendency to swell<sup>9</sup>.

The polymerization of methacrylonitrile in solution in solvents of polymethacrylonitrile gives homogeneous solutions, from which the polymerized product can be separated by precipitating agents. Whereas the solutions are light yellow like the products of mass polymerization, the products which are precipitated as described above are pure white. In agreement with experience with solution polymerization of other unsaturated compounds, products with lower degrees of polymerization than those obtained by mass polymerization under otherwise identical conditions are obtained.

When methacrylonitrile is polymerized in nonsolvents of the polymer, *e.g.*, in toluene, the polymerized product separates out in swollen form. It is soluble in solvents like acetone.

Table 1 summarizes data on polymers obtained by mass polymerization. As a means of characterizing the products in a qualitative way, there are included, in addition to the concentration of catalyst (benzoyl peroxide) and temperature and time of polymerization, the specific viscosity  $\eta_{sp}/c$  in very

TABLE I

CONDITIONS OF POLYMERIZATION, SPECIFIC VISCOSITY, AND AVERAGE DEGREE OF POLYMERIZATION OF METHACRYLONITRILE POLYMERS OBTAINED BY MASS POLYMERIZATION.

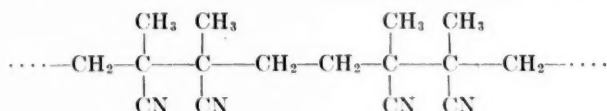
Product	Concentration of benzoyl peroxide (percentage)	Temperature of polymerization (° C)	Time of polymerization (hours)	$\eta_{sp}/c$	Average degree of polymerization
1	1	100	38	0.0095	140
2	3	82	48	0.0293	450
3	5	60	80	0.0528	820
4 <sup>10</sup>	1.75	60	100	0.0570	900
5	4	60	80	0.0594	940
6	3	60	100	0.0705	1150
7 <sup>10</sup>	2	60	96	0.103	2000
8 <sup>10</sup>	1.75	60	150	0.116	2460
9 <sup>10</sup>	2	60	112	0.117	2480
10 <sup>10</sup>	2	60	118	0.121	2640
11	1.5	60	112	0.209	7500 (approx.)
12	1	62	240	0.229	9500 (approx.)

dilute acetone solution and the average degree of polymerization, as obtained from osmotic and viscometric measurements (see Figure 3).

Since the products listed in Table I are polymer fractions which were obtained at 60° C, it might be thought that a correction factor for polymers no. 1 and no. 2, which were prepared at 100° C and 82° C, respectively, should be introduced. However, it was decided to disregard this correction, since it has been shown that, in contrast to polystyrenes<sup>11</sup>, the ratio ( $K_m$  constant) of the specific viscosity and degree of polymerization determined osmotically is for polyvinyl chloride<sup>12</sup> and methyl polymethacrylate<sup>13</sup> independent of the temperature of polymerization. It can therefore, be assumed that polymethacrylonitrile behaves similarly to methyl polymethacrylate. In estimating the degree of polymerization, account must also be taken of the fact that curve II in Figure 3, which represents the relation between specific viscosity and degree of polymerization, was drawn from data on fractionated products, and that the products shown in Table I are unfractionated polymers.

#### PROPERTIES OF POLYMETHACRYLONITRILES

Unlike polyacrylonitriles, polymethacrylonitriles are soluble in a series of organic solvents, and can therefore be studied by ordinary methods of macromolecular chemistry. In analogy with acrylic esters and methacrylic esters<sup>14</sup>, the structure of their macromolecules can be assumed to be as follows:



Some of the properties of polymethacrylonitriles which were investigated are shown in Table 2, in comparison with properties of polyacrylonitrile.

Elementary analysis of polymethacrylonitrile shows too low values for carbon and nitrogen, although highly purified methacrylonitrile was used for the analysis<sup>15</sup>. It made little difference whether the polymerization was carried

TABLE 2  
PROPERTIES OF POLYACRYLONITRILE AND POLYMETHACRYLONITRILE

Property	Polyacrylonitrile	Polymethacrylonitrile
Appearance	White to yellow, powdery or brittle mass	Colorless to pale yellow, glassy, transparent blocks
Mechanical behavior	Pulverizable	Hard; not brittle; very difficult to pulverize.
Softening point	Not definite	Approximately 115° C
Decomposition point	Approximately 350° C	Approximately 200° C
Solubility in concentrated sulfuric acid	Partial saponification	Partial saponification
Solubility in organic solvents	Insoluble and no tendency to swell in any organic solvent tested	Swells and dissolves in acetone, benzonitrile, methylene chloride, and cyclohexanone. Hemicolloids also soluble in tetrahydrofuran, nitrobenzene

out under nitrogen or in a high vacuum, or whether the polymer was dissolved and reprecipitated<sup>16</sup> (see Table 3).

TABLE 3  
ELEMENTAL ANALYSIS OF POLYMETHACRYLONITRILES

Element	Polymerization of methacrylonitrile at 60° C			After single solution and reprecipitation of I	Calculated value $C_4H_5N + 1\%$ benzoyl peroxide
	under air I	under nitrogen II	in a high vacuum III		
Carbon	70.29	70.73	71.0	70.57	71.61
Hydrogen	7.51	7.52	7.53	7.42	7.43
Nitrogen	19.49	19.10	20.03	19.62	20.68

It is difficult to find a reason for the low carbon and nitrogen values. However, it is at least evident that polymerization in a high vacuum gave the best product. Nor can these results be more than partially explained by the splitting off of hydrogen cyanide, which was observed in the previous work<sup>17</sup>.

In contrast to this, carefully fractionated polymethacrylonitriles (see Figure 4) give much better analytical data (see Table 4); yet here too the values for carbon and nitrogen are still too low.

TABLE 4  
ELEMENTAL ANALYSES OF SIX FRACTIONS OF A POLYMETHACRYLONITRILE

Fractions	I	II	III	IV	V	VI	Calculated value for $C_4H_5N$
Average degree of polymerization (osmotic in acetone)	approx. 20,000	4030	1750	690	400	310	
Carbon	71.32	71.25	71.28	71.12	71.41	71.09	71.64
Hydrogen	7.75	7.48	7.53	7.57	7.57	7.45	7.46
Nitrogen	20.28	20.32	20.68	20.44	21.48	21.29	20.90

For polyvinyl chloride Staudinger and Schneiders<sup>12</sup> found a chlorine content which was approximately 0.5–1 per cent too low. The parallelism with polyacrylonitrile and polymethacrylonitrile is unmistakable.

## FRACTIONATION OF POLYMETHACRYLONITRILE

An homologous series of polymers can be obtained by varying the conditions of the polymerization reaction<sup>18</sup>. However, homologous polymers which have been obtained by fractionation are much more suitable for investigation, for it can be safely assumed that the structures of the molecular chains of fractions obtained from a polymerized product are similar, irrespective of their average degrees of polymerization, and therefore that these fractions are homologous polymers.

In this fractionation, acetone was found to be a particularly suitable solvent, for in the subsequent drying of the product it is easily removed. Methanol or low-boiling petroleum ether can be used to advantage as a precipitating agent. The fractions are obtained by precipitation with methanol from an approximately 1 per cent solution in acetone, in which case the methanol is added dropwise, with attendant stirring. Fractionation was carried out by the procedure described by Schulz<sup>19</sup>, and each fraction was redissolved and reprecipitated. In this way the products were obtained in powdery or fibrous form, and could be easily filtered and dried.

TABLE 5

FRACTIONS OF A POLYMETHACRYLONITRILE, THEIR SPECIFIC VISCOSITIES, AND THEIR MOLECULAR WEIGHTS, DETERMINED OSMOTICALLY

Product	Proportion of each fraction (percentage by weight) <sup>20</sup>	$\left( \frac{\eta_{sp}}{c} \right)_{c \rightarrow 0}$	Average degree of polymerization (osmotic)	Average molecular weight (osmotic)
Unfractionated polymer <sup>21</sup>	100	0.116	2460	165,000
Fraction I	20.5	0.350	20,000 (approx.)	1,340,000
Fraction II	10.3	0.150	4030	270,000
Fraction III	10.2	0.0945	1750	117,000
Fraction IV	30.5	0.0451	690	46,000
Fraction V	20.5	0.0270	400	26,800
Fraction VI	8.0	0.0210	310	20,800

Table 5 shows the fractions of a polymethacrylonitrile which were used in further investigations. Here are shown the proportions of the various fractions, the average degrees of polymerization and molecular weights (determined osmotically) and the limiting values of the specific viscosity  $(\eta_{sp}/c)_{c \rightarrow 0}$  in acetone.

## OSMOTIC MEASUREMENTS OF POLYMETHACRYLONITRILES

In determining the molecular weight of polymethacrylonitrile, osmotic measurements of acetone solutions were carried out by the method of Schulz, with evaluation by the methods of limits<sup>22</sup> and volume correction<sup>23</sup>. The results which were obtained by the two methods are in excellent agreement. As a result of extensive experiments on a large number of macromolecular compounds<sup>24</sup>, it seems probable that the weights of the particles are the actual molecular weights.

The measurements are summarized in Table 6. In Figure 1,  $p/c$  is plotted as a function of the concentration. From this the limiting values of  $p/c$  for  $c = 0$  can be read, and these can likewise be estimated from the data in Table 6. In Figure 2, the effective volume  $s$  is plotted on a logarithmic scale as a function of the osmotic pressure  $p$ . It can be shown that the equation<sup>25</sup>:  $p = k \cdot s^{-r}$



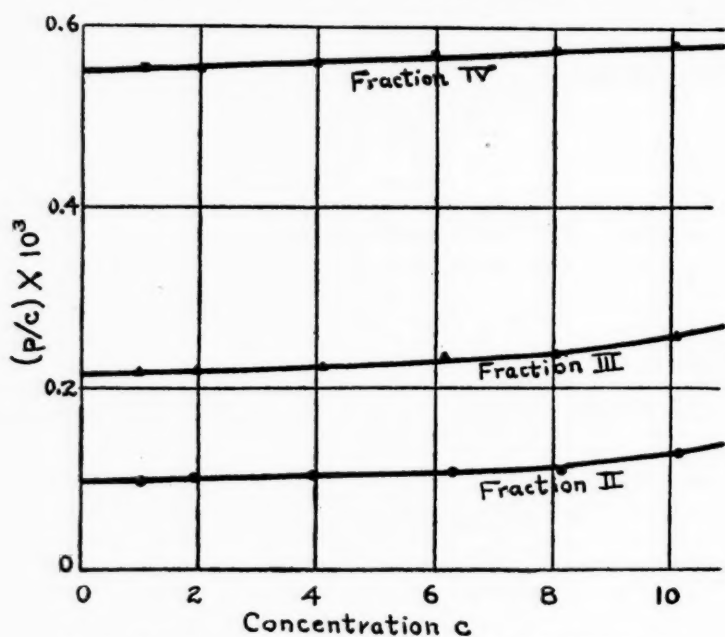


Fig. 1.—Osmotic pressure  $p/c$  of three polymethacrylonitriles in acetone at 27° C as a function of the concentration  $c$  in grams per liter.

TABLE 6

OSMOTIC MEASUREMENTS OF POLYMETHACRYLONITRILES IN ACETONE AT 27° C.  
DETERMINATION OF THE AVERAGE MOLECULAR WEIGHTS

Product <sup>25</sup>	Concentration $c$ (g. per liter)	$p \times 10^3$	$(p/c) \times 10^3$	Effective volume $S^{28}$	Average molecular weight <sup>27</sup>	Average degree of polymerization
Fraction II	0.00	—	0.095	—	259,000	3860
	1.01	0.096	0.095	0.050	273,000	
	1.90	0.183	0.096	0.037	275,000	
	3.94	0.400	0.102	0.025	268,000	
	6.29	0.649	0.103	0.020	273,000	
	8.14	0.885	0.109	0.017	262,000	
	10.14	1.29	0.127	0.015	(229,000)	
Fraction III	Average				270,000	4030
	0.00	—	0.215	—	114,000	1730
	0.99	0.214	0.216	0.034	118,000	
	1.95	0.428	0.219	0.024	118,000	
	4.09	0.916	0.224	0.017	118,000	
	6.14	0.143	0.233	0.014	116,000	
	8.06	1.91	0.237	0.012	115,000	
	10.09	2.60	0.257	0.011	(108,000)	
Fraction IV	Average				117,000	1750
	0.00	—	0.550	—	45,000	670
	1.06	0.587	0.554	0.021	45,400	
	2.03	1.12	0.556	0.016	45,800	
	3.97	2.22	0.560	0.011	45,900	
	5.95	3.39	0.570	0.009	45,600	
	8.03	4.57	0.570	0.008	46,200	
	10.05	5.74	0.570	0.007	46,500	
Average					46,000	690

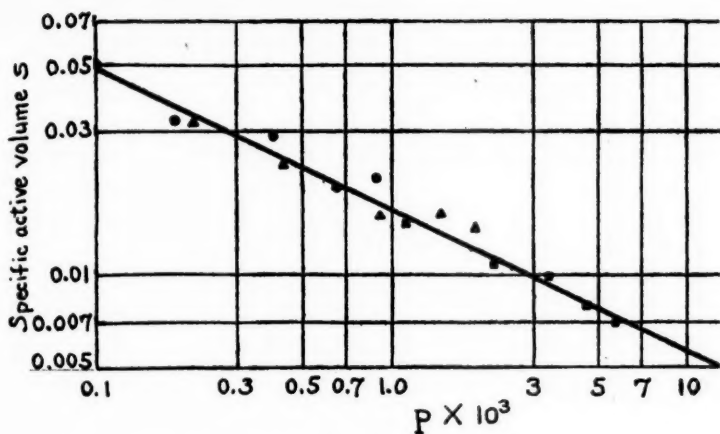


Fig. 2. Osmotic pressure  $p$  of three polymethacrylonitriles as a function of the specific volume  $s$ : Fraction II ● Fraction III ▲ Fraction IV ■

is valid for the homologous series of polymethacrylonitriles as well as for a whole series of linear macromolecular compounds. The results show in addition that the molecular weights of polymethacrylonitriles may be very high.

#### VISCOMETRIC MEASUREMENTS OF POLYMETHACRYLONITRILES

##### SPECIFIC VISCOSITY AND MOLECULAR SIZE

It was to be expected that viscometric measurements of solutions of polymethacrylonitriles might throw further light on the size and form of their macromolecules. The influence of the form of macromolecules on the viscosity of solutions is now well-known as a result of investigations by Staudinger<sup>28</sup>. Mention may be made only of glycogen, with spherical molecules, which follows the viscosity law of Einstein, and of cellulose, with linear molecules, which follows the viscosity law of Staudinger. In the case of substances with strictly linear macromolecules, the simple equation of Staudinger is valid over a considerable range. It has, however, been found that polyvinyl and polyacryl compounds show deviations of considerable magnitude from this law<sup>29</sup>. When determined osmotically, the degree of polymerization has been found to be considerably higher than the value corresponding to the equation:  $\eta_{sp}/c = K_m \cdot P$ . Furthermore the  $K_m$  values show a characteristic trend in that they decrease with increase in molecular size. This same relation is also shown by polymethacrylonitriles.

The  $K_m$  values are summarized in Table 7.

TABLE 7

$K_m$  VALUES OF POLYMETHACRYLONITRILES AS A FUNCTION OF THE AVERAGE DEGREE OF POLYMERIZATION (ACETONE AS SOLVENT AND TEMPERATURE 20° C)

Product <sup>30</sup>	$\eta_{sp}/c$	Average degree of polymerization (osmotic)	$K_m$
Fraction II	0.150	4030	$0.37 \times 10^{-4}$
Fraction III	0.0945	1750	$0.54 \times 10^{-4}$
Fraction IV	0.0451	690	$0.65 \times 10^{-4}$

Although the relation between molecular size and specific viscosity is not a linear one, a functional relation between viscosity measurements and molecular-weight measurements can nevertheless be shown<sup>31</sup>. This can best be done by plotting by means of a few points the curve representing specific viscosity  $\eta_{sp}/c$  as a function of average degree of polymerization (determined osmotically). Thus the measurements recorded in Table 7 give curve II in Figure 3.

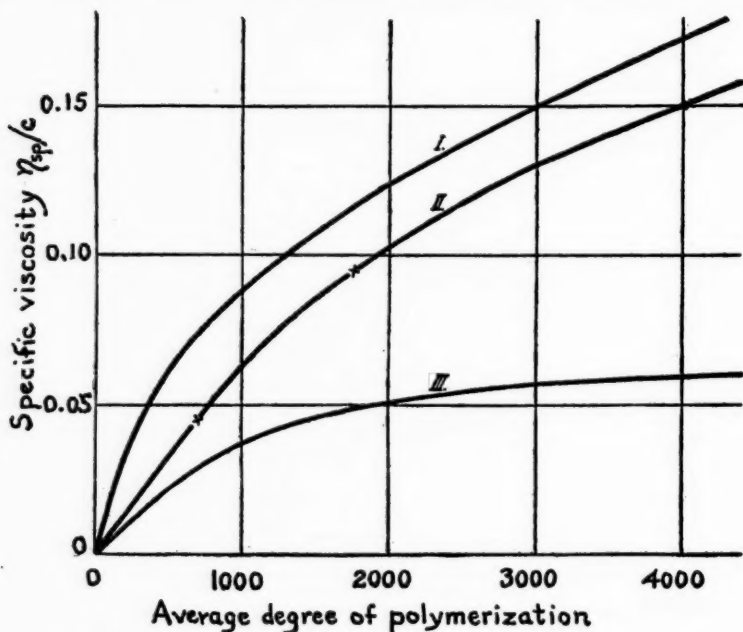


FIG. 3.—Specific viscosity  $\eta_{sp}/c$  of three polymers as a function of the average degree of polymerization, determined osmotically.

The degrees of polymerization of fractions I, V and VI (Table 5) were estimated by means of curve II<sup>32</sup>. It is worthy of note that the curves of polyvinyl chloride (I)<sup>31</sup> and polymethacrylonitrile (III) have very similar courses, and that the curve of polymethacrylonitrile lies between the curve of polymethyl methacrylate (III) and the curve of polyvinyl chloride (II)<sup>31</sup>, both of which are likewise shown in Figure 3.

Little can be said as to the reason why the viscosity equation of Staudinger does not hold true of polymethacrylonitriles. Polymerized products are now known, *e.g.*, polystyrenes<sup>33</sup>, at least fractions of which follow the viscosity law of Staudinger. Furthermore, other substances are known where there is a parallelism between the specific viscosity and molecular size, yet where the relation is by no means linear<sup>34</sup>.

#### VISCOSITY AS A FUNCTION OF CONCENTRATION

The dependence of the specific viscosity on the concentration was studied by means of three polymethacrylonitriles in acetone<sup>35</sup> (Table 8).

The relation between specific viscosity and concentration shows a trend similar to that of other polyvinyl compounds, *e.g.*, polystyrene<sup>36</sup>. In the case

TABLE 8

SPECIFIC VISCOSITY  $\eta_{sp}/c_0$  AS A FUNCTION OF CONCENTRATION. MEASUREMENTS OF THREE POLYMETHACRYLONITRILES IN ACETONE AT 20° C

Fraction I		Fraction II		Fraction III	
Average degree of polymerization approx. 20,000 $K_S = 2.9$		Average degree of polymerization approx. 4030 $K_S = 1.5$		Average degree of polymerization approx. 570 $K_S = 0.65$	
$c_0^*$	$\eta_{sp} = c_0$	$c_0$	$\eta_{sp} = c_0$	$c$	$\eta_{sp} = c_0$
0.00	23.5	0.0	10.0	0.0	2.50
0.017	25.8	0.024	11.0	0.014	2.48
0.045	29.2	0.070	12.9	0.029	2.68
0.081	34.5	0.158	16.7	0.059	2.88
0.131	53.8	0.213	20.8	0.108	3.02
0.181	78.4	0.350	32.8	0.185	3.28
0.302	172.0	—	—	0.243	3.55
—	—	—	—	0.359	4.09

\*  $c_0$  = base molecular concentration;  $c_0 = c/G_m$ ;  $G_m$  = base molecular weight = 67 for polymethacrylonitrile

of polymers of relatively low molecular weight, the specific viscosity  $\eta_{sp}/c$  is nearly constant over a wide range of concentrations. On the contrary, in the case of polymers of high molecular weight, the specific viscosity increases greatly with increase in concentration, even with very dilute solutions. When the logarithms of the specific viscosity are plotted against the base molecular concentration, straight lines are obtained (see Figure 4). Accordingly poly-

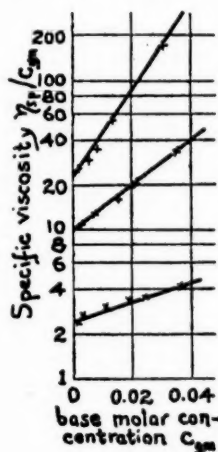


FIG. 4.—Specific viscosity  $\eta_{sp}/c_{gm}$  (logarithmic) of three polymethacrylonitriles in acetone (see Table 8) as a function of the base molar concentration  $c_{gm}$ .

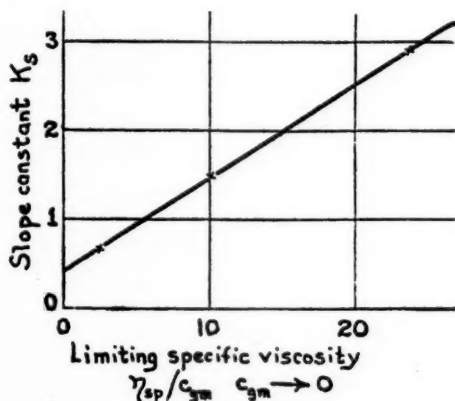


FIG. 5.—Slope constants  $K_S$  of polymethacrylonitriles in acetone as a function of the limiting values of the specific viscosity (see Table 8).

methacrylonitriles conform well to the viscosity-concentration law established by de Jong, Kruyt and Lens<sup>37</sup> and by Staudinger and Heuer<sup>36</sup>.

$$\log \frac{\eta_{sp}}{c_0} = \log \left( \frac{\eta_{sp}}{c_0} \right)_{c_0 \rightarrow 0} + K_S \cdot c_0 \quad (2)$$

For the slope constant<sup>38</sup>,  $K_S$ , Staudinger and Heuer<sup>36</sup> found the following relation to hold true of polystyrenes:

$$K_S = K_{MS}M + b \quad (3)$$

Since the slope constants have been found to be independent of both the solvent and the prevailing temperature, their determination serves as a basis for a particularly advantageous method for estimating molecular size. On the other hand this relation does not hold true of polymethacrylonitriles, which do however conform to the following relation:

$$K_S = K_{MS} \left( \frac{\eta_{sp}}{c_g} \right)_{c_g \rightarrow 0} + b \quad (4)$$

Similar relations apply to polystyrenes and polymethacrylonitriles. Since in the case of polymethacrylonitriles there is no proportionality between specific viscosity and molecular weight, it is possible for Equation (4) to be valid, and yet Equation (3) to be invalid at the same time.

#### DEPENDENCE OF THE SPECIFIC VISCOSITY OF THE TEMPERATURE AND ON THE SOLVENT

The dependence of the specific viscosity on the temperature was determined with cyclohexanone solutions at 20° C and 60° C. As with other linear molecular colloids, this functional relation is independent of the degree of polymerization. Staudinger and Heuer<sup>39</sup> found the quotient  $[\eta_{sp}/c(60^\circ \text{C})]/[\eta_{sp}/c(20^\circ \text{C})]$  to be 0.84 for polystyrenes, and Staudinger and Schneiders<sup>40</sup> found this quotient to be 0.91 for polyvinyl chloride. For polymethacrylonitriles, this quotient has a mean value of 0.86 (see Table 9).

TABLE 9

DEPENDENCE OF SPECIFIC VISCOSITY ON TEMPERATURE. POLYMETHACRYLONITRILES IN CYCLOHEXANONE AT 20° AND 60° C

Product	Average degree of polymerization	$\eta_{sp}/c$ (20° C)	$\eta_{sp}/c$ (60° C)	$\frac{\eta_{sp}/c(60^\circ \text{C})}{\eta_{sp}/c(20^\circ \text{C})}$
Fraction I	20,000 (approx.)	0.519	0.448	0.87
Fraction II	4,030	0.215	0.181	0.85
Fraction III	1,750	0.127	0.108	0.86
Fraction IV	690	0.0618	0.0518	0.84
Fraction V	400	0.0360	0.0308	0.86
Fraction VI	310	0.0281	0.0240	0.86

The dependence of the specific viscosity on the solvent was studied by means of solutions in cyclohexanone and acetone. The cyclohexanone solutions were more viscous than the acetone solutions. Cyclohexanone is, therefore, in the sense employed by Staudinger<sup>36</sup>, a better solvent than acetone for polymethacrylonitriles. Furthermore in the case of both cyclohexanone and acetone, the quotient of the specific viscosities was found to be nearly independent of the degree of polymerization (see Table 10).

#### SAPONIFICATION OF POLYMETHACRYLONITRILES

When polymethacrylonitriles are saponified, polymethacrylic acids are obtained as products. It was hoped to be able to carry out this reaction under conditions such that polymerically analogous products would be formed<sup>41</sup>, i.e., products having the same average degree of polymerization as that of the

TABLE 10  
SPECIFIC VISCOSITIES OF POLYMETHACRYLONITRILES IN CYCLOHEXANONE  
AND IN ACETONE AT 20° C

Product	Average degree of polymerization	$\eta_{sp}/c$ in cyclohexanone	$\eta_{sp}/c$ in acetone	(acetone) (cyclohexanone)
Fraction I	20,000 (approx.)	0.519	0.350	0.68
Fraction II	4,030	0.215	0.150	0.70
Fraction III	1,750	0.127	0.0945	0.74
Fraction IV	690	0.0618	0.0451	0.73
Fraction V	400	0.0360	0.0270	0.75
Fraction VI	310	0.0280	0.0210	0.75

starting material. However, polymethacrylonitriles can be saponified only under very energetic conditions, *e.g.*, by hot 40 per cent sodium hydroxide solution. Under these conditions polymethacrylic acids containing nitrogen are obtained, which it is not right to assume have withstood the treatment without decomposition.

Saponification of the polymethacrylonitriles by 40 per cent sodium hydroxide solution was carried out while hot, and in pure nitrogen. The ammonia which was liberated was absorbed in dilute sulfuric acid and determined quantitatively. Products formed by mass polymerization, which were in the form of fine powders, were found to be more difficult to saponify than redissolved and reprecipitated products. The degree of saponification of a redissolved, reprecipitated polymer was 67 per cent after about 6 hours' reaction with boiling 40 per cent sodium hydroxide. By still longer boiling it was found possible to increase the degree of saponification to over 80 per cent.

When saponified, polymethacrylonitriles passed into solution, leaving behind in many cases a residue which, judged by analysis, consisted essentially of unchanged starting material. The solutions from the saponification reactions were diluted with water, separated from the residues mentioned above, and neutralized by an acid. The resulting polymethacrylic acids were then precipitated by glacial acid<sup>42</sup>. Even after being purified, these polymethacrylic acids contained nitrogen.

$C_4H_6O_2$	Calculated	C 55.81	H 6.98	N —
	Found	52.86	7.56	2.73

The nitrogen content of this polymethacrylic acid corresponds to a content of unsaponified nitrile groups of 12.5 per cent. It is also possible that the nitrogen which did not split off was present in some other form, but it is most likely that these nitrile groups were merely not saponified.

The saponification of polymethacrylonitrile to a polymethacrylic acid proceeds with much greater difficulty than the saponification of polyacrylonitrile to polyacrylic acid<sup>17</sup>. There is an unmistakable analogy to polymethacrylic esters and polyacrylic esters. Derivatives of polyacrylic acid can be saponified with greater ease than can derivatives of polymethacrylic acid. Yet on the basis of the solubilities of the two polynitriles, just the opposite would be expected.

#### THERMAL DECOMPOSITION OF POLYMETHACRYLONITRILE

A methacrylonitrile polymer with an average degree of polymerization of approximately 800 was heated in the dry state without exclusion of air. At about 115° C a clearly defined softening point was observed, and when the



heating was continued, the product, which was originally bright yellow, turned deep red. At 250° C vapors were evolved, and these could be easily condensed. The heating was continued until the residue was carbonized. By this method approximately 85 per cent of monomeric methacrylonitrile was obtained<sup>43</sup>. This indicates that polymethacrylonitrile can be depolymerized to a considerable degree, with reversion to monomeric methacrylonitrile. When prepared in this way, the latter was found to be pure after two successive careful fractionations.

Analysis gave the following results.

C <sub>4</sub> H <sub>5</sub> N	Calculated	C 71.64	H 7.46	N 20.90
	Found	71.62	7.61	20.63

It polymerized in the same way as pure methacrylonitrile<sup>44</sup>.

In its extensive depolymerization to the monomer, polymethacrylonitrile shows a parallelism to polymethyl methacrylate, and a great contrast to polyacrylonitrile, which yields no trace of its monomer when decomposed thermally.

Consequently, not only when saponified but also when decomposed thermally, derivatives of polymethacrylic acid behave both similarly to, and very differently from, the corresponding derivatives of polyacrylic acid. The methyl group in  $\alpha$ -position has, therefore, a decisive influence on the chemical behavior of these polymers.

#### ACKNOWLEDGMENT

The present investigation and the preceding one<sup>17</sup> were carried out in the chemical laboratories of the Universities of Freiburg i. Br. and Frankfurt a. M. The authors are particularly indebted to Professor Staudinger, who carried on the work while one of the authors (W. Kern) was called into the armed services. They are also indebted to the Government Ministry for the Development of Commerce, the Höchst works of the I. G. Farbenindustrie A.-G. and the Röhm und Haas-Ges., Darmstadt, who lent financial and material support to the investigation, and to the Justus Liebig-Ges. for its aid in making possible the chemical training through the grant of a scholarship to one of the authors (H. Fernow).

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- <sup>2</sup> English patent 416,007; *Chem. Zentr.* 1935, II, 1445.
- <sup>3</sup> English patent 424,885; *Chem. Zentr.* 1936, I, 2439.
- <sup>4</sup> Bruylants, Ernould and Dekoker (*Bull. Acad. Roy. Belg., Classe Sciences* [5] 16, 721 (1930)) prepared  $\alpha$ -methylcrotononitrile from methylethylketonecyanohydrin by this method. Rohm and Haas Co., Philadelphia (U. S. patent 2,210,320) used this same method and obtained similar yields, but their patent did not appear until the work of the present authors was completed.
- <sup>5</sup> French patent 794,255; *Chem. Zentr.* 1936, I, 4074.
- <sup>6</sup> Signer and Gross, *Ann.* 488, 56 (1931) obtained cyclohexene by thermal decomposition of the cyclohexanol ester of orthosilicic acid.
- <sup>7</sup> Mertens and Fonteyn, *Congr. chim. ind. Bruxelles* 15, 870 (1935).
- <sup>8</sup> Usually the solubility of a macromolecular substance is determined by treating samples of the substance with the solvent concerned. By then precipitating with a nonsolvent it can be ascertained whether all or at least part of the substance has dissolved. The present authors have used another method which has given very good results, and which requires only that a solvent for the substance be known. A solution of the substance in this solvent is treated with a precipitating agent until the solution becomes turbid. If to this turbid solution is added a solvent of the substance, the turbidity disappears immediately because of solution of the suspended substance. On the contrary if a nonsolvent is added, precipitation takes place. This method has the advantage that a large number of liquids can be tested for their solvent power in a very short time.
- <sup>9</sup> With respect to polystyrenes with limited tendency to swell, see Staudinger and Heuer, *Ber.* 67, 1164 (1934); Staudinger and Husemann, *Ber.* 68, 1618 (1935). With respect to methyl polymethacrylate, see Staudinger and Warth, *J. prakt. Chem.* [2] 155, 261 (1940).
- <sup>10</sup> Additions of approximately 20 grams of methacrylonitrile. All other products were obtained from additions of 1 gram.
- <sup>11</sup> Staudinger and Schulz, *Ber.* 68, 2332 (1935); Schulz and Husemann, *Z. physik. Chem.* 36B, 184 (1937).
- <sup>12</sup> Staudinger and Schneiders, *Ann.* 541, 151 (1939).

- <sup>12</sup> Staudinger and Warth, *J. prakt. Chem.* [2] **155**, 261 (1940).
- <sup>13</sup> Marvel and Cowan, *J. Am. Chem. Soc.* **61**, 3156 (1939); Marvel and Levesque, *J. Am. Chem. Soc.* **61**, 3244 (1939).
- <sup>14</sup> For analysis, see the first section of this paper.
- <sup>15</sup> The approximately 1 per cent acetone solution was allowed to flow into methanol.
- <sup>16</sup> Kern and Fernow, *J. prakt. Chem.* **160**, 281 (1942); RUBBER CHEM. TECH. **17**, 356 (1944).
- <sup>17</sup> See for example the polymers in Table 1.
- <sup>18</sup> Schulz, *Z. physik. Chem.* **30B**, 379 (1935); **46B**, 137 (1940); *J. prakt. Chem.* [2] **155**, 115 (1940).
- <sup>19</sup> With account taken of the slight losses occurring in the fractionation operations.
- <sup>20</sup> Product VIII in Table 1.
- <sup>21</sup> Ostwald, *Kolloid-Z.* **49**, 60 (1929).
- <sup>22</sup> Schulz, *Z. physik. Chem.* **176A**, 317 (1936).
- <sup>23</sup> Staudinger, "Organische Kolloidchemie", Vieweg & Sohn, 2nd Ed., **1941**, p. 140; Kern and Houwink, "Chemie und Technologie der Kunststoffe", Akad. Verl.-Ges. Leipzig, 2nd Ed., **1942**, p. 126.
- <sup>24</sup> These fractions are the same as designated in Table 5. Only fractions II, III and IV were studied, because fraction I had too high a molecular weight, so the effects were too small to be measured. On the contrary fractions V and VI had too low molecular weights, and their diffusion through the membranes was a disturbing factor.
- <sup>25</sup> Based on the corrected values in Figure 2. The  $s$  values in Figure 2 are calculated by the equation  $s = (1/c) - RT/(p \cdot M)$ , for fraction II with average molecular weight 273,000, fraction III with average molecular weight 117,500, and fraction IV with average molecular weight 46,000.
- <sup>26</sup> The average molecular weights were calculated by the equation:  $M = R \cdot T \cdot c/[p(1 - c \cdot s)]$ , where the values in column 4 of Table 6, corrected according to Figure 2, are substituted for  $s$ . The average values shown in Table 6 for the mean molecular weights and mean degrees of polymerization were used as a basis in these calculations.
- <sup>27</sup> Staudinger, "Organische Kolloidchemie", Vieweg & Sohn, Braunschweig, 2nd Ed., **1941**, p. 201.
- <sup>28</sup> Staudinger, "Organische Kolloidchemie", Vieweg & Sohn, Braunschweig, 2nd Ed., **1941**, pp. 189, 217.
- <sup>29</sup> These fractions are the same as those designated in Tables 5 and 6.
- <sup>30</sup> Staudinger, "Organische Kolloidchemie", Vieweg & Sohn, Braunschweig, 2nd Ed., **1941**, p. 193.
- <sup>31</sup> The degree of polymerization of the polymer in Table 1 was determined in the same way. Since in the present case unfractionated polymers are concerned, the molecular-size distribution of which differs from the fractions, the average degrees of polymerization in Table 1 are somewhat uncertain.
- <sup>32</sup> Staudinger and Schulz, *Ber.* **68**, 2332 (1935); Schulz and Dinglinger, *J. prakt. Chem.* **158**, 136 (1941).
- <sup>33</sup> Schulz and Dinglinger, *J. prakt. Chem.* **158**, 136 (1941). Unfortunately it is not possible to evaluate accurately osmotic and viscometric measurements by the equation of Kuhn (*Angew. Chem.* **49**, 858 (1936)), as carried out by Houwink (*J. prakt. Chem.* [2] **157**, 15 (1940)) with measurements of Staudinger and Warth (*J. prakt. Chem.* [2] **155**, 261 (1940)), since the number of osmotic measurements is too small (see Table 7). However, in agreement with data on polyvinyl acetates, polyvinyl alcohols, polyacrylic esters and polymethacrylic esters, the exponent  $n$  of the Kuhn equation:  $\eta_{sp}/c = K \cdot M^n$  is approximately 0.6 for polymethacrylonitriles, i.e., it is of the same magnitude as found by Houwink for the polymers mentioned.
- <sup>34</sup> Solutions of polymethacrylonitriles are not sensitive to air; therefore the measurements can be carried out without any special precautions.
- <sup>35</sup> Staudinger and Heuer, *Z. physik. Chem.* **171A**, 129 (1934).
- <sup>36</sup> de Jong, Kruyt and Lens, *Kolloidchem. Beih.* **36**, 441 (1932).
- <sup>37</sup> The values of  $K_S$  and  $(\eta_{sp}/c)_{c \rightarrow 0}$  are given in Table 8.
- <sup>38</sup> Staudinger and Heuer, "Die hochmolekularen organischen Verbindungen", Julius Springer, Berlin, **1932**, p. 174.
- <sup>39</sup> Staudinger and Schneiders, *Ann.* **541**, 151 (1939).
- <sup>40</sup> Staudinger, "Organische Kolloidchemie", Vieweg & Sohn, Braunschweig, 2nd Ed., **1941**, p. 164.
- <sup>41</sup> Kern, *Biochem.-Z.* **301**, 338 (1939).
- <sup>42</sup> A distinct odor of aliphatic amine was also perceptible.
- <sup>43</sup> Methacrylonitrile, which was prepared by decomposition of polymethacrylonitrile, and which was not carefully fractionated, gave in many cases insoluble polymers with limited tendency to swell. See in this connection the data of Staudinger and Warth (*J. prakt. Chem.* [2] **155**, 261 (1940)) on polymethylmethacrylate.

## THE STRUCTURE OF POLYISOPRENES. II.

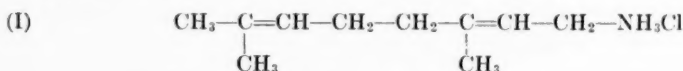
### THE STRUCTURE OF $\beta$ -GUTTA-PERCHA\*

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The ultimate goal in studying the crystal structures of polyisoprenes is the complete picture of the atomic arrangements in the crystal lattices. This can be attained by the synthesis of results from experimental observations on the polyisoprenes themselves and on substances variously related to them. From the detailed x-ray analysis of simple crystalline compounds, precise geometrical data about the molecules become available which point to the probable stereochemistry of the polymers. The criterion of the validity of a proposed polymer structure is that it shall be based on well-founded and self-consistent principles, and shall account for the x-ray diffraction measurements from the polymer as rigorously as this limited information allows.

The crystal structure analysis of a simple diisoprene derivative, geranylamine hydrochloride (I)<sup>1</sup>, provides a basis for a model of the translinked polyisoprene molecule,  $\beta$ -gutta-percha. This model differs significantly in molecular detail from that proposed by Bunn<sup>2</sup>, although it accounts equally well for his observed x-ray intensities on the fibre diagram. The interpretation of these intensities has therefore been reexamined, and it has become clear that such data alone cannot determine molecular details of high polymers uniquely, and so should not be relied upon to support structures involving bond distortions for which there is no other evidence.



*The  $\beta$ -Gutta-percha Model.*—The  $\beta$  modification of gutta-percha is the simplest natural polyisoprene to consider, since the fibre-axis length of 4.7 to 4.8 Å. U. reveals a repeating unit along the hydrocarbon chain compatible only with one *trans* isoprene group. Assuming the bond lengths and angles of the  $\text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2$  group to be normal and the distribution of C—C valencies



about the double bond to be planar, in agreement with both the geranylamine structure and general chemical theory, there remain two variables, the orientation and length of the  $\text{CH}_2 - \text{CH}_2$  bond. As the steric environment is the same, with the same barriers to free rotation about the C—CH<sub>2</sub> bond, as in the geranylamine molecule, the same angle of 80° to the isoprene plane can be expected in the crystalline state. Although this may be influenced to some extent by the intermolecular packing in the crystal lattice, the deviation must be small to avoid unbalanced repulsions between the CH<sub>2</sub> and the CH or CH<sub>3</sub> groups.

\* Reprinted from the *Transactions of the Faraday Society*, Vol. 40, Part 11, pages 517–520, November 1944.

This factor was appreciated by Bunn when, selecting for his model a smaller value of this angle ( $63^\circ$ ), he also introduced a large bond distortion of the methyl group out of the plane of the double bond valencies ( $24^\circ$ ), and ascribed it to just such a steric repulsion<sup>3</sup>.

The length of the  $\text{CH}_2\text{—CH}_2$  bond in the geranylamine hydrochloride molecule was observed to be shorter than normal. As the electronic process responsible for this bond shortening is still imperfectly understood, it cannot be applied directly to the polymer. However, for the purpose of this exploratory approach to the interpretation of the fibre-diagram, two models were considered: one in which the  $\text{CH}_2\text{—CH}_2$  length was  $1.45 \text{ \AA. U.}$ , and the  $\text{C—CH}_2\text{—CH}_2$  angle  $112^\circ$  as in geranylamine; a second with a normal  $\text{C—C}$  value of  $1.54 \text{ \AA. U.}$  and the tetrahedral angle.

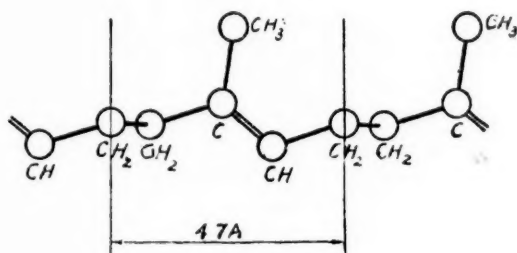


FIG. 1.

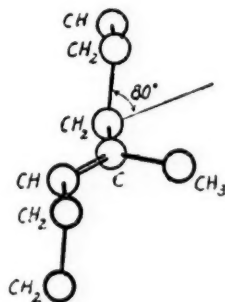


FIG. 2.

*Application to the Crystal Structure.*—Accepting, as consistent with the best available experimental evidence, the cell dimensions, space group and general crystal structure proposed by Bunn<sup>2</sup>, the two models described above were adjusted in the unit cell to positions in which the atomic coördinates gave a satisfactory agreement between the calculated and observed intensities. The intensities were calculated from the formulas for the space group  $P_{212121}$ <sup>4</sup>, with appropriate geometrical factors. The carbon atomic scattering factors used were those derived experimentally from the geranylamine structure, and although the two structures are from the point of view of thermal agitation not strictly comparable, these are considered adequate for the purpose of comparison with observations of a qualitative nature. The  $\left(f_c, \frac{\sin \theta}{\lambda}\right)$  curve was similar in shape to the theoretical one compiled by James and Brindley<sup>5</sup>, with a Debye-Waller temperature factor of  $B \times 10^{16} = 2.0$ .

The atomic parameters for the normal model are given in Table I, together

TABLE I  
ATOMIC COÖRDINATES

	<i>x</i>	<i>y</i>	<i>z</i>	
C <sub>1</sub>	0.076	0.109	0.453	CH <sub>2</sub>
C <sub>2</sub>	0.019	0.071	0.155	CH
C <sub>3</sub>	0.978	0.145	0.953	C
C <sub>4</sub>	0.921	0.107	0.654	CH <sub>2</sub>
C <sub>5</sub>	0.987	0.274	0.995	CH <sub>3</sub>
bond lengths	C—C	1.54 Å. U.,	C=C	1.33 Å. U.
bond angles	C—C—C	122°,	C—C—C	109°

with the interatomic dimensions. The intensity values calculated from these parameters are shown in Table II for comparison with the observed intensities

TABLE II

<i>hkO</i>	<i>I</i> <sub>calc.</sub>	<i>I</i> <sub>obs.</sub>	<i>hkl</i>	<i>I</i> <sub>calc.</sub>	<i>I</i> <sub>obs.</sub>	<i>hk2.</i>	<i>I</i> <sub>calc.</sub>	<i>I</i> <sub>obs.</sub>
110	0	—	011	93	ms	112	1	w
020	1	vw	101	0	—	022	10	
120	538	vs+	111	11	vw	122	3	—
200	295	vs	021	1	—	032	1	w
210	2		121	10	—	202	8	
130	0	—	031	24	w	212	2	
220	3	vw	201	4		132	5	
040	39	m	211	69	ms	222	12	—
230	1	ms	131	10		042	0	—
140	59		221	1	—	232	3	—
310	0	—	041	3	—	142	1	—
320	17	m	231	11	vw			
240	11		141	2				
150	0	—	301	1	w			
330	0	—	311	9				
250	0	—	321	3	—			
060	7	w	051	0	—			
340	4	w	241	4	—			
400	6		151	0	—			
410	1	m	331	6	—			
160	19		251	0	—			
420	1	—	061	1	—			
260	4	vww	341	0	—			
350	0		401	1	—			
430	1	—	411	14	w			
170	0	—	161	1	—			
440	0	—	421	1	—			
360	2	vww						
270	0	—						

recorded by Bunn. The corresponding figures for the model containing the shorter CH<sub>2</sub>—CH<sub>2</sub> bond are very similar, and the small differences in the calculated intensities would be of significance only when compared with accurate measurements.

### CONCLUSIONS

Although the general position of the molecule in the unit cell is necessarily similar, the normal model differs stereochemically from that proposed by Bunn in two important respects: (1) planar distribution of the C—C bonds about the double bond, with no distortion of the methyl group out of the plane; (2) orientation of the CH<sub>2</sub>—CH<sub>2</sub> bond at 80° as against 63° to the plane of the double bond. Despite these differences, the agreement between the observed and calculated diffraction data is at least as good. This result shows that there is no justification for the premise that the x-ray data demand an unusually large distortion in the molecule of  $\beta$ -gutta-percha<sup>3</sup>, and it also supports the criticisms<sup>6</sup> advanced on more general considerations of Bunn's crystal structure of rubber<sup>2</sup>. Similarly, the bond angle distortions recorded for polychloroprene<sup>2</sup> and rubber hydrochloride<sup>7</sup> cannot be regarded as real in the absence of confirmatory evidence.

The structure for  $\beta$ -gutta-percha discussed above, although inherently more probable than that proposed by Bunn, is not regarded as a final solution. Together with further evidence from indirect sources, it will provide a starting

point for a precise x-ray investigation of these polymers when the technical difficulties of extending the diffraction data from fibre diagrams and expressing them more quantitatively have been overcome.

#### SUMMARY

The x-ray diffraction data at present available from  $\beta$ -gutta-percha are shown to be insufficient to distinguish fine details of molecular structure. Since a qualitative estimate of the intensities on the fibre diagram can be adequately satisfied by a model having normal interatomic distances and valency angles, no evidence exists for the improbable distortion of the methyl group out of the plane of the double bond previously ascribed to the molecule.

#### ACKNOWLEDGMENT

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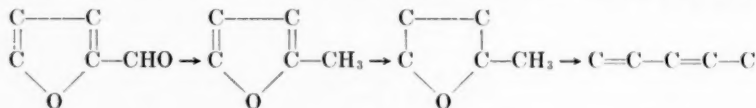


# THE PRODUCTION OF RUBBER FROM FURFURAL\*

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The preparation of piperylene, or 1,3-pentadiene, from furfural has been undertaken with the view of developing a commercially practical process. Although other paths are possible, the following three steps were considered the most direct and feasible. During the course of this study, a patent<sup>1</sup> was granted which covered essentially the same process, but the claims, particu-



larly of the last two steps, were not substantiated in this laboratory.

Vapor-phase catalytic reactions were utilized in the process. For the first two steps, a vapor phase hydrogenation apparatus with a recirculation device was employed. This effected the saving of considerable quantities of hydrogen and uncondensed materials. The apparatus could also be employed for the dehydration in the last step.

More than twenty catalysts were studied for the conversion of furfural to methylfuran (sylvan). Only two types were found to be satisfactory. The copper deposited from the decomposition of copper acetate on a carrier such as activated charcoal was found to give yields of the order of 80-85 per cent consistently with one passage of the furfural over the catalyst. The best catalyst tried, however, was copper chromite dispersed on activated charcoal. This has been observed to give a yield of 95 per cent of sylvan in one passage. The optimum temperature observed for these catalysts was around 200° C. It is interesting to note that copper chromite in the liquid phase produces furfuryl alcohol (or tetrahydrofurfuryl alcohol according to the conditions used) in quantitative amounts<sup>2</sup>.

Such an efficient conversion of furfural to sylvan applied commercially would make this compound available in large quantities at a low price. With such a stimulus, it should find many important industrial applications. It boils at 64° C, has a refractive index of 1.433<sup>20</sup>, and a density of 0.916<sup>20</sup>.

The vapor phase hydrogenation of sylvan to tetrahydrosylvan was studied over several types of nickel catalysts. One of the more effective of these was partially activated Raney nickel. After determining that Raney nickel activated in the usual way led to ring opening and other undesired reactions, Raney nickel activated with only 6-8 per cent of the usual amount of sodium hydroxide was used with much better results. The best yields obtained, however, were of the order of 50 per cent. Besides the desired tetrahydrosylvan, 2-pentanone and 2-pentanol were identified in the product in appreciable quan-

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tities. Tetrahydrosylvan boils at 78°–79°, has a refractive index of 1.4059<sup>21</sup>, and a density of 0.8534<sup>21</sup>.

The dehydration of tetrahydrofurans has been the subject of at least two patents<sup>3</sup>, in which yields of dienes as high as 85 per cent have been claimed. Although the reaction was not exhaustively studied in this laboratory, trials with five different dehydration catalysts have given yields up to only 30 per cent of piperylene. From the amount of water formed, more than twice this much dehydration was indicated, but it is presumed that the yield of the 1,3-fraction was decreased both by the formation of the isomeric 1,4-pentadiene and by decomposition of the desired product.

By carrying out the dehydration at a pressure of 60–85 mm., less decomposition and higher yields were obtained. In the case of the kaolin catalyst studied at a temperature of 400° C, the yield of piperylene at atmospheric pressure was 17 per cent. At a lower pressure of about 70 mm. a yield of 30 per cent was obtained.

Piperylene (b.p. 42° C,  $n$  1.440<sup>16</sup>,  $d$  0.696) was first observed to polymerize to a rubber by Thiele<sup>4</sup> in 1901. Since then, a limited amount of work has been reported in the literature regarding this property. Nothing current has appeared, however, which would serve to compare its properties with the present synthetic rubbers. This research is a necessary precursor to the application of the process on a commercial scale. In this laboratory an emulsion polymerization process similar to that used for butadiene has been used to prepare a satisfactory rubber from piperylene.

The potentially huge quantities of furfural annually available (estimated at 50,000,000 tons) have been emphasized in many instances. Assuming the utilization of but 21 per cent of the annual corn cob crop and mediocre yields in the reactions under discussion, it has been estimated that 100,000 tons of piperylene could be produced at a maximum cost of \$.38 per pound, and at a probable cost much lower than this. This price compares favorably with the current prices of other synthetic rubbers.

In addition to the attractive price, the waste materials utilized in the furfural process are much less critical than the grain and petroleum resources now used. This, even more than cost considerations, should be the deciding factor in its adoption.

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# THE MECHANISM OF REINFORCEMENT

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## INTRODUCTION

While the question of a fundamental theory of rubber elasticity is still hotly debated and far from solved, the formal treatment of pigment "reinforcement" has recently made encouraging advances.

Rehner<sup>1</sup>, Smallwood<sup>2</sup>, and still more recently Guth<sup>3</sup> have brought the problem to the point where, at least, ground for discussion exists. Smallwood has derived an equation for the change of modulus of an elastomer under the influence of a dispersed filler. This equation is similar to that of Einstein<sup>4</sup> for the viscosity of a liquid in which solid particles are suspended. Guth has also described the modulus of a "filled" rubber stock by an equation similar to the viscosity expression, with the addition of the squared term to the two terms used by Smallwood. This equation is as follows:

$$E = E_0(1 + 2.5c + 14.1c^2) \quad (1)$$

where  $E$  is the modulus of elasticity of the filled sample in terms of the modulus of elasticity of the pure medium  $E_0$  and the volume concentration  $c$  of the filler. The assumptions made are:

- (1) that the suspended particles are spherical;
- (2) that the suspended particles are small compared to the total sample;
- (3) that the suspended particles are large compared to the discontinuity of the elastic medium;
- (4) that the elastic medium is firmly attached to the particles.

If Smallwood's results are plotted according to Equation (1), a good check is observed for the experimental points (Figure 1), with the exception of channel blacks at higher loadings. In this last case the experimental moduli are considerably greater than those predicted by the present theory. This indicates clearly that carbon black is a "reinforcing" pigment which induces more pronounced changes in rubber properties than most other fillers. Equation (1) is fundamentally sound within the limits of applicability. These limits seem to be fulfilled by carbon black and rubber at lower loadings; hence the reasons for the discrepancy at higher loadings must be examined closely. It is evident that discrepancies between Equation (1) and experiment may be ascribed to the following: first,  $c$ , the volume concentration of the carbon black in the stock may not correspond to that calculated directly from the weight and density of the added black and, secondly,  $E_0$ , the modulus of elasticity of rubber between particles of black may not be the same as that of the pure-gum stock.<sup>5</sup>

The concept of carbon-bound rubber has long been recognized<sup>6</sup>. Goldfinger and Smith<sup>7</sup> have shown that the electric conductivity of rubber loaded with carbon black can be predicted with the aid, among others, of the concept

of rubber surrounding the carbon particle in a tight layer comparable in size to the dimensions of the carbon particle. Finally electron-microscope pictures<sup>8</sup> substantiate this concept. Hence Guth has recently concluded that  $c$  should be replaced in Equation (1) by  $c_1$ , the actual volume loading, which is the volume of carbon black  $c$ , increased by that of the associated rubber layer.

So far, no method is known for establishing a reliable value of  $E_0$ . With some justification the modulus of elasticity of pure-gum stock is usually taken for  $E_0$ ; this, however, may be a source of error. The retarding influence of carbon black on the rate of vulcanization of accelerated stocks is well known, and as yet there is no means of identifying a state of cure of a pure-gum stock equivalent to that of a stock compounded with carbon black. The "optimum" cure, usually selected, may be fallacious, for the presence of the highly active carbon surface may cause considerable change in concentration and distribution of the curing agent, or indeed may change the mechanism of cure altogether<sup>9</sup>.

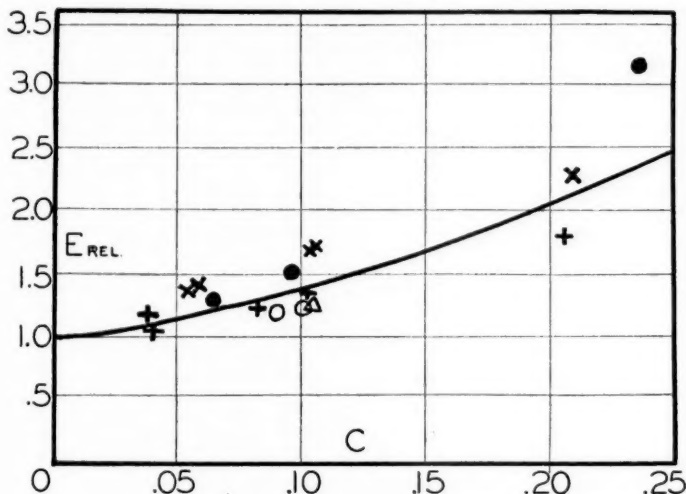


Fig. 1.—Experimental data of Smallwood indicated by: ● Channel black; ○ P-33, Thermax; × Kadox, XX zinc oxide; + Gilders whitening; Δ Catalpo clay. The curve is drawn from Equation (1).

Furthermore from preliminary experiments described below, it appears that carbon black adsorbs preferentially a fraction in rubber, and increases the modulus of the unadsorbed fraction. Hence  $E_0$  as determined from the pure-gum stock should be replaced by a value  $E_0'$  representing the modulus of the medium.

To determine the influence of carbon black on the physical properties of that fraction of the rubber which is *not* in intimate contact with the pigment, some preliminary experiments have been carried out. In one experiment carbon black was mixed with a rubber cement and then removed by centrifuging. The viscosity of the clear, centrifuged material was compared with that of the original untreated rubber cement. In another experiment the rubber was recovered by precipitation from the original cement and also from the cement after treatment with carbon black. The stress-strain properties of these two samples of reclaimed rubber were then compared.

## EXPERIMENTAL

About 120 grams of commercial GR-S was milled for 30 minutes at 5° C on a 2" × 6" Thropp two-roll mill. Two 60-gram samples of the stock thus obtained were placed in each of two one-gallon jugs and 3000 cc. of CP toluene was added to each. The two jugs were then rotated for 24 hours at room temperature. Fifteen grams (20 per cent by weight of rubber) of Cabot Easy-Processing Channel Black (surface area 100 sq. m. per g.; average diameter from E. M. count, 316 Å. U.; volatile 5.1 per cent) was added to the cement in one jug. Both jugs were then rotated for 48 hours. After this extended rotation the carbon black-treated sample showed good dispersion. After standing for one week at room temperature, samples were taken from each jug. On analysis the sample of carbon black-GR-S cement was found to have a carbon black loading of 16.8 per cent by weight, based on the GR-S content.

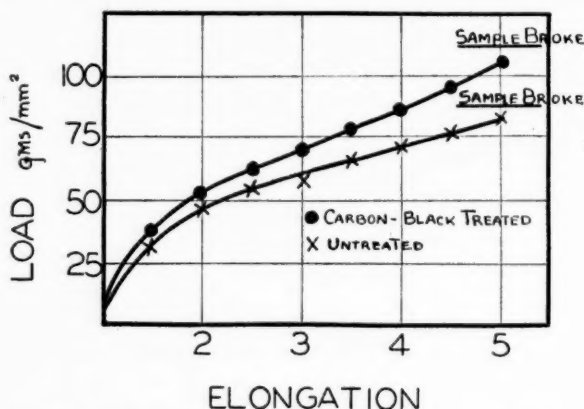


Fig. 2.—Load-elongation for rubber samples recovered from solution.

The carbon black-GR-S cement was then centrifuged in a Sorvall centrifuge<sup>10</sup> at 5400 to 5500 rev. per min. (maximum centrifugal force about 3500 to 4000 times gravity) for 20 minutes. After this treatment the supernatant liquid had a carbon black content of 3.20 per cent, based on rubber. This supernatant liquid was further diluted with toluene in the ratio 950 cc. of cement to 1000 cc. of toluene, and centrifuged further for two hours. This treatment removed from the cement all but 0.9 per cent of the residual carbon black (0.5 per cent by volume). The GR-S was then precipitated by pouring this centrifuged cement into 10-fold the volume of methanol. After mechanically squeezing out most of the methanol, the precipitated GR-S was placed in an all-glass vacuum oven, evacuated to less than  $10^{-3}$  mm. Hg, and heated to 77° C (boiling point of carbon tetrachloride) for 6 hours. The content of material volatile at that temperature was less than 0.1 parts in 100, as determined on a control sample. This identical procedure, with the exception of the centrifuging, was then repeated with the sample of GR-S cement which had not been treated with carbon black. This sample served as a blank.

Both the GR-S recovered after treatment with carbon black and the blank were then compounded on a 2" × 6" roll mill as follows: 8.0 grams of rubber; 2 minutes on cold (5° C) tight rolls; 1.80 grams of master batch added, and milled 8 minutes. The master batch had the composition: GR-S 30, sulfur 3,

Santocure 1.8, Bardol 9, and zinc oxide 9 parts. Compound no. 1 and Compound no. 2 were prepared as follows:

Compound no. 1	Recovered GR-S	8.010	Compound no. 2	Recovered GR-S	8.015
	Master batch	1.804		Master batch	1.800

After 24 hours the samples were sheeted out and cured 90 minutes at 144° C in two of the four inner compartments of a 16-cavity 2' × 2.5' × 0.1" mould. After 24 hours of further aging, 2' long "T-50" strips were cut, and the load-elongation was measured on a Scott tensile machine. For these measurements the stress measuring balance was replaced by an electric strain gauge set to a sensitivity of one scale division for 5.41 grams load. On a repeat test the greatest deviation observed was that of one scale division. The results are given in Figure 2.

The results show that the GR-S sample recovered from the cement treated with carbon black has a higher modulus and tensile strength than the sample

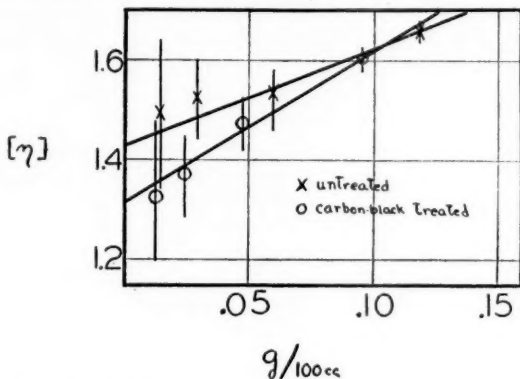


Fig. 3.—Specific viscosity vs. concentration for treated and untreated samples.

The straight lines correspond to the "best" lines.

prepared from the untreated cement. The modulus and tensile strength values of both samples, however, are extremely low. This is not astonishing in view of the treatment the samples received before testing. However, extreme care was taken in the preparation of the treated sample and the blank to insure maximum uniformity of treatment with respect to unknown factors. Accordingly, although the absolute values obtained are not significant, the differences between the two samples are real. Ultimate elongation is not given for the samples, since the apparatus employed for the measurement did not permit reliable determination of this quantity. However, the elongation of the carbon black-treated sample appeared to be slightly greater than that of the blank. A further sample of the carbon black-treated GR-S cement was spun at 7400 revolutions in an 11 cm. radius Sorvall centrifuge (6000 times gravity) for one more hour. This gave an entirely transparent, though colored cement. An electron-microscope examination of this cement indicated absence of carbon black. The GR-S concentration of this cement and of the blank was determined by evaporating the toluene at 110° C and weighing. The cements were then diluted with toluene to various concentrations ranging from 1 to .01 gram of GR-S per 100 cc. The viscosities were measured at 26.2° C in an Ostwald pipette. The results are plotted in Figure 3 as intrinsic viscosities,



where intrinsic viscosity is expressed by the following relation:

$$\text{Intrinsic viscosity} = \frac{\frac{\text{time of flow of solution}}{\text{time of flow of solvent}} - 1}{\text{concentration}}$$

These measurements show, at concentrations below 0.1 gram per 100 cc., a considerably steeper slope for the carbon black-treated sample.

### INTERPRETATION

From the experiments and the results described above, it is obvious that some preferential adsorption of polymer around the carbon black particles occurs. The first and most intriguing explanation would be that the branched fraction of GR-S is adsorbed preferentially on the carbon surface, and hence the material as recovered from the carbon black-treated solution contains a considerably higher fraction of linear polymer than the original material contained. However, in view of recent results by Kemp and Straitiff,<sup>11</sup> such an interpretation seems doubtful. Kemp found that the most easily precipitated fraction of rubber, which probably contains not only the highest molecular weight fraction of the linear polymer but also the bulk of the branched material<sup>12</sup>, shows higher values for modulus and tensile strength. However, the fact seems to be established that, under the influence of "reinforcing" pigments, at least with carbon black, such a fractionation of the rubber occurs as to leave a tougher material between particles than the average of the original material. Further investigation in this laboratory is designed to throw more light on the nature of this fraction and on the mechanism of the preferential adsorption.

### SUMMARY

In the fundamental study of the influence of reinforcing pigments, particularly carbon black on rubber, one of the great experimental difficulties is to establish the stress-strain properties of that fraction of the rubber stock which is between the pigment particles, and whose deformation, influenced by the presence of the pigment, is the quantity desired. This paper shows that it is not justifiable to assume that the rubber between pigment particles is equivalent in properties to the original gum stock without pigment, because the addition of pigment induces fractionation of the rubber in such a manner as to concentrate preferentially one molecular configuration around the pigment particle, and hence leave the rubber richer in some other configuration in the spaces between pigment particles.

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- <sup>4</sup> Einstein, *Ann. Physik* 19, 289 (1906); 34, 591 (1911); generalized by Guth and Gold, *Phys. Rev.* 53, 322 (1938).
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$$E = E_0(1 + k_1 f c_1 + k_2 f^2 c_1^2) \quad (1')$$

where  $f$  is the axis ratio of the carbon-black chains or clusters. The author is indebted to E. Guth

for a discussion of the problem, particularly for this communication, which has not yet been published.

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# LIMITING LAW OF THE REINFORCEMENT OF RUBBER\*

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## INTRODUCTION

An obvious theoretical approach to the reinforcement of rubber is to analyze the stresses about a filler particle, and from this analysis to deduce the effect of particle size and concentration of filler on the modulus. Because of the great similarity between the field equations of the theory of elasticity and those of hydrodynamics, this approach is substantially the same as that employed by Einstein<sup>1</sup> in the discussion of increase in viscosity caused by suspension of spherical particles in the liquid.

## THEORY

Consider a rigid, spherical particle of radius  $a$  embedded in rubber of known modulus. We now suppose that the rubber is stretched, and will calculate the displacements and stresses in the vicinity of the solid particle, resulting from this stretch.

The differential equations of equilibrium may be put in the following form:

$$\begin{aligned}\frac{\lambda + \mu}{\mu} \frac{\partial \nabla}{\partial x} + \nabla^2 u &= 0 \\ \frac{\lambda + \mu}{\mu} \frac{\partial \Delta}{\partial y} + \nabla^2 v &= 0 \\ \frac{\lambda + \mu}{\mu} \frac{\partial \Delta}{\partial z} + \nabla^2 w &= 0\end{aligned}\tag{1}$$

In these equations<sup>2</sup>  $x, y, z$  are the customary Cartesian coördinates, and  $u, v, w$  are the vector components of displacement at the point  $x, y, z$ .  $\Delta$  is the cubical dilation and  $\nabla^2$  is the Laplacian operator.  $\lambda$  and  $\mu$  are the elastic constants of the rubber, and are related to Young's modulus  $M$  and Poisson's ratio  $\sigma$  by the expressions:

$$\begin{aligned}M &= \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \\ \sigma &= \frac{\lambda}{2(\lambda + \mu)}\end{aligned}$$

To attack the problem it is necessary to specify the boundary conditions to be fulfilled. The first of these arises from the fact that the influence of the

\* Reprinted from the *Journal of Applied Physics*, Vol. 15, No. 11, pages 758-766, November 1944. This paper was presented at the Inaugural Meeting of the Division of High-Polymer Physics of the American Physical Society, Rochester, N. Y., June 23, 1944.

particle extends only through a limited region of the rubber. At points far distant from the particle, the displacements correspond to those caused by a simple tension. The second boundary condition is that the displacement at the surface of the solid sphere must vanish, since we assume that there is complete adhesion between rubber and filler particle. These boundary conditions may be expressed algebraically by the following equations: at  $r = \infty$

$$\begin{aligned} u &= -\frac{\lambda T}{2\mu(3\lambda + 2\mu)} x = -Cx \\ v &= -\frac{\lambda T}{2\mu(3\lambda + 2\mu)} y = -Cy \end{aligned} \quad (2a)$$

$$w = +\frac{(\lambda + \mu)T}{\mu(3\lambda + 2\mu)} z = Az$$

at  $r = a$ :

$$u = v = w = 0 \quad (2b)$$

Here  $T$  is the tension in the rubber at an infinite distance from the filler particle. The origin of coordinates has been located at the center of the solid sphere, and the  $Z$  axis oriented parallel to the direction of stretch. These boundary conditions completely specify the problem. The solution for the displacements is obtained in the form:

$$\begin{aligned} u &= -x \left\{ C \left( 1 - \frac{a^3}{r^3} \right) - B \frac{a^3}{r^3} \left( 1 - \frac{a^2}{r^2} \right) \left( 1 - 5 \frac{z^2}{r^2} \right) \right\} \\ v &= -y \left\{ C \left( 1 - \frac{a^3}{r^3} \right) - B \frac{a^3}{r^3} \left( 1 - \frac{a^2}{r^2} \right) \left( 1 - 5 \frac{z^2}{r^2} \right) \right\} \\ w &= x \left\{ A \left( 1 - \frac{a^3}{r^3} \right) + B \frac{a^3}{r^3} \left( 1 - \frac{a^2}{r^2} \right) \left( 3 - 5 \frac{z^2}{r^2} \right) \right\} \end{aligned} \quad (3)$$

where

$$r^2 = x^2 + y^2 + z^2$$

and

$$B = \frac{3}{4} \frac{T}{\mu} \frac{\lambda + \mu}{3\lambda + 8\mu}$$

To apply these results to rubber, it is convenient to introduce the assumption that Poisson's ratio equals  $\frac{1}{2}$ , as is known to be the case for rubber at small elongations. This assumption is incorporated in our equations by setting  $\lambda$  infinitely large compared to  $\mu$ . Then:

$$\begin{aligned} A &= \frac{1}{3} \frac{T}{\mu} \\ B &= \frac{1}{4} \frac{T}{\mu} \\ C &= \frac{1}{6} \frac{T}{\mu} \end{aligned} \quad (4)$$

Reference to Equation (2a) shows that, in our notation, Young's modulus equals  $3\mu$  when  $\lambda \gg \mu$ .

To obtain the total effect of the filler particle, it is necessary to form the strain energy function  $W$ , and to integrate  $W$  throughout the volume of the rubber. By carrying out this operation, we obtain:

$$\int_v W dV = \frac{T^2}{2\mu} \left\{ \frac{1}{3} \left( V - \frac{4}{3} \pi a^3 \right) + \frac{1}{2} \cdot \frac{4}{3} \pi a^3 \right\} \quad (5)$$

where  $V$  is the total volume of the rubber plus that of the particle. For  $N$  particles per unit volume, the average energy per unit volume becomes:

$$\begin{aligned} \bar{W} &= \frac{T^2}{2\mu} \left( \frac{1}{3} + \frac{1}{6} \cdot N \cdot \frac{4}{3} \pi a^3 \right) \\ &= \frac{T^2}{2} \frac{1}{3\mu} \left( 1 + \frac{1}{2} \Phi \right) \\ &= \frac{A^2 M}{2} \left( 1 + \frac{1}{2} \Phi \right) \end{aligned} \quad (6)$$

where  $\Phi$  is the fractional volume loading calculated on the total volume of the mix, and  $M$  is Young's modulus of the rubber matrix. In agreement with this equation, Weiss<sup>3</sup> and Rehner<sup>4</sup> have recently concluded that the energy of deformation of compounded rubber is independent of the particle size of the filler.

We now wish to determine the sum of the effects at some arbitrary point in the rubber owing to all the filler particles. We may rewrite the last member of Equation (2a) in the following form:

$$w_0 = Az \quad (7)$$

where  $z$  is now a coordinate referred to an arbitrary zero, located in the rubber matrix, with the  $Z$  axis parallel to the direction of stretch. We now suppose that the filler particles are distributed uniformly throughout the rubber, and that they are so far apart that their effects on the point  $x, y, z$  are small compared to  $u_0, v_0, w_0$ . Then:

$$w = +Az + \sum w_n \quad (8)$$

where  $w_n$  is the modification in the  $Z$  component of the displacement owing to the  $n$ th particle. We can obtain the overall modulus by bringing this last equation to the form:

$$w = \bar{A}z \quad (9)$$

Substituting for  $w_n$  from Equation (3), after transformation to the new coordinates, and replacing the summation with an integration, we find:

$$\begin{aligned} \bar{A} &= A \left( 1 - N \cdot \frac{4}{3} \pi a^3 \right) \\ &= A(1 - \Phi) \end{aligned} \quad (10)$$

The average energy  $\bar{W}$  is related to the constant  $\bar{A}$  by the equation:

$$\bar{W} = \frac{\bar{A}^2 M^*}{2} \quad (11)$$

where  $M^*$  is Young's modulus of the compounded stock, i.e., the overall modulus. Equation (6) gives us, however, another value for  $\bar{W}$ . By equating

these two expressions, and substituting for  $\bar{A}$  from (10), we find:

$$\frac{\bar{A}^2 M^*}{2} = \frac{A^2(1 - \Phi)^2 M^*}{2} = \frac{A^2 M}{2} (1 + \frac{1}{2}\Phi)$$

Cancelling and dividing through by  $(1 - \Phi)^2$ , we find:

$$M^* = M(1 + 2.5\Phi) \quad (12)$$

on neglecting higher powers in  $\Phi$ .

This last equation is the desired result. Its content may be expressed in words by the statement that the relative modulus ( $M^*/M$ ) is directly proportional to the volume loading, and is independent of particle size of the filler. The factor of proportionality, 2.5, is the same as that found by Einstein for the viscosity of a suspension.

There is some interest attached to a calculation of the stress system in the vicinity of the filler particle. The results may be written in the following form, using spherical coordinates with origin at the center of the particle and polar axis in the direction of stretch:

$$\begin{aligned} \hat{r}r &= \left\{ \frac{1}{3} - (1 - \cos^2 \vartheta) \left( \frac{1}{3} + \frac{5}{2} \frac{a^3}{r^3} - 2 \frac{a^5}{r^5} \right) \right\} T \\ \hat{\vartheta}\vartheta &= \left\{ 1 - \cos^2 \vartheta - (3 - 7 \cos^2 \vartheta) \frac{a^5}{r^5} \right\} T \\ \hat{\varphi}\varphi &= -\frac{T}{2} (1 - 5 \cos^2 \vartheta) \frac{a^5}{r^5} \\ \hat{r}\vartheta &= -T \sin \vartheta \cos \vartheta \left( 1 - \frac{5}{2} \frac{a^3}{r^3} + 4 \frac{a^5}{r^5} \right) \\ \hat{r}\varphi &= \hat{\vartheta}\varphi = 0 \end{aligned} \quad (13)$$

Here  $\hat{r}r$  is the radial component of the stress acting on a plane perpendicular to the radius vector.  $\hat{\vartheta}\vartheta$  is the component, along the  $\vartheta$  coordinate direction, of the stress acting on a plane perpendicular to this direction. A similar definition holds for  $\hat{\varphi}\varphi$ . The remaining stress components (for example,  $\hat{r}\vartheta$ ) represent the radial component of the stress acting on a plane perpendicular to the  $\vartheta$  coordinate direction, etc.

We are most interested in the forces tending to separate the rubber from the filler particle. These are derived from the above equations by setting  $r = a$ . Then:

$$\begin{aligned} \hat{r}r &= -\frac{1}{2} (1 - 5 \cos^2 \vartheta) T \\ \hat{\vartheta}\vartheta &= -\frac{5}{4} T \sin 2\vartheta \end{aligned} \quad (14)$$

From the foregoing, we see that the normal stress at the interface is a maximum at the poles of the particle, that is, when  $\vartheta = 0$  or  $180^\circ$ . At these points the stress is equal to twice the tension in the rubber matrix at a large distance from the filler particle. As  $\vartheta$  increases from 0 to  $90^\circ$  the normal stress decreases from twice the tension in the rubber at  $\vartheta = 0$  to zero at  $\vartheta = 63^\circ 26'$ . The normal stress then changes from tension to compression, and increases in



magnitude up to  $\vartheta = 90^\circ$ , at which point it is equal to the tension  $T$ . The shearing component is zero both at the poles and around the equator of the particle. When  $\vartheta$  goes from 0 to  $90^\circ$  the shearing component increases to a maximum at  $45^\circ$  and then decreases again to 0. The maximum shearing stress at  $\vartheta = 45^\circ$  is equal to 1.25 times the tension in the rubber.

It must be emphasized that the foregoing equations are valid only for infinitely small displacements. Of course the strains in rubber in the interesting range are far from being infinitely small. However, the results just described remain qualitatively correct for the case of finite strains, *i.e.*, the normal component of force at the poles will always be greater than the tension in the rubber matrix. Furthermore, the particle will always experience a compression along the equatorial region, and shearing stresses at intermediate points. This, of course, is what one would expect.

A further limitation to the preceding calculations is the fact that we have assumed the filler particles to be spherical. When this is not the case, it may be expected that the stresses tending to separate the rubber from sharp points or corners near the poles are considerably greater than those indicated by the calculation.

### EXPERIMENTS

Data sufficient to give an adequate test of these calculations are not available in the literature. To obtain such a test, we need measurements of the modulus at zero elongation of a series of stocks containing low volume loadings of various fillers, and prepared in such a way that the modulus of the rubber matrix is known. Since the effects we wish to measure are rather small (10 per cent volume loading should cause only a 25 per cent increase in modulus), it is necessary that the measurements be of a high degree of accuracy. The following experiments were, therefore, performed.

A complete formula for a gum stock was mixed. Into portions of this master batch were milled varying proportions of the fillers to be investigated. The different samples were then cured, and it was assumed that the modulus of the rubber matrix in the compounded stocks was the same as that of the gum stock cured from the same master batch when the samples were at the same state of cure. When this assumption is fulfilled, it is possible to obtain a direct check on the validity of Equation (12). As will be seen, however, this basic assumption was not always valid. Precautions were taken to subject the pure gum blank to milling and storage conditions identical with those which were employed for the compounded stocks.

Most of the experiments were carried out on a simple mercaptobenzothiazole mix containing 3 parts of sulfur. A few measurements were also made on a base mix containing Hepteen accelerator and 3 of sulfur, with no zinc oxide. The fillers investigated were carbon black, P-33 black, Thermax black, Kadox zinc oxide, XX zinc oxide, gilders' whiting, and Catalpo clay. In some cases additional mercaptobenzothiazole was added to the carbon black stocks to counteract the retarding effect of this filler. Formulas are given in Table I.

The amount of filler added was checked throughout the bulk of the experiments by weighing the master batch as soon as it had been broken down on the mill, incorporating the filler, and then weighing the completed mix again. The weights of filler added were obtained by difference.

To obtain the desired accuracy, special test-pieces measuring  $\frac{1}{4} \times \frac{1}{4} \times 24$  inches were prepared. Stocks were calendered, and 13 plies were plied up to a thickness of  $\frac{1}{4}$  inch. Strips  $\frac{3}{8}$  inch wide were cut from these sheets and placed

TABLE I

## FORMULAS

FORMULAS								
	<i>SLS</i>	<i>SLT</i>	<i>SLU</i>					
Blended pale crepe A	100	—	—					
Hepteen	2	—	—					
Sulfur	3	—	—					
SLS	—	105	105					
Gilders' whiting	—	13	27					
Cured 45-60-75-90 min. at 40 lbs. steam								
	<i>SMN</i>	<i>SMO</i>	<i>SMP</i>					
Blended pale crepe A	100	—	—					
Kadox zinc oxide	1	—	—					
Laurex	3	—	—					
Mercaptobenzothiazole	0.5	—	—					
Sulfur	3	—	—					
SMN	—	107.5	107.5					
Thermax black	—	21	—					
Channel black	—	—	21					
Mercaptobenzothiazole	—	—	0.2					
Cured 45-60-75-90 min. at 30 lbs. steam								
	<i>L</i>							
Blended pale crepe A	100							
Kadox zinc oxide	1							
Laurex	3							
Mercaptobenzothiazole	0.5							
Sulfur	3							
Cured 30-45 min. at 30 lbs. steam								
	<i>M</i>							
Unbroken down pale crepe	100	} Master batch for samples N-AB						
Kadox zinc oxide	1							
Laurex	3							
Mercaptobenzothiazole	0.5							
Sulfur	3							
	<i>N</i>	<i>O</i>	<i>P</i>	<i>R</i>	<i>S</i>	<i>T</i>	<i>U</i>	<i>V</i>
M	107.5	107.5	107.5	107.5	107.5	107.5	107.5	107.5
Channel black	47.5	10	—	—	—	—	—	—
P-33 black	—	—	21	—	—	—	—	—
Catalpo clay	—	—	—	31	—	—	—	—
Gilders' whiting	—	—	—	—	—	15	32	72
Captax	0.7	0.5	—	—	—	—	—	—
			<i>W</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>AA</i>	<i>AB</i>
M			107.5	107.5	107.5	107.5	107.5	107.5
Kadox zinc oxide			—	32	67	—	—	—
XX zinc oxide			—	—	—	32	67	152
Cured 45-60-75-90 min. at 30 lbs. steam								

edgewise in the mold. This gave an unusually large overflow and resulted in complete filling of the mould and elimination of air bubbles.

Measurements of modulus were made in the following manner.

Each sample was first weighed to the nearest centigram, and then given a standard massage of 20 stretches to about 100 per cent elongation. The width and thickness of the sample were then gauged in several places and the averages recorded. The length of the specimen was also measured in each case. To obtain accurate bench marks two needles were then inserted, one near each end, and perpendicular to the long axis. The sample was then mounted in a clamp so that the protruding points of the needles rested against the scale

of a meter stick. After reading the initial distance between the needle points, various loads from 0.5 to 1.5 kilograms were applied to the lower end of the test-piece. After application of each load, the test-piece was oscillated about its point of equilibrium and the positions of the needle points were read. The resulting observations gave, therefore, a reversible stress-strain curve according to Gerke's technique<sup>5</sup>. After application of the highest load in each series of measurements, the weight was removed and the length of the test-piece at zero load again determined, to insure the absence of appreciable set.

In general, only three points were taken on the stress-strain curve of each sample, the maximum elongation varying from 10 to 30 per cent. Preliminary experiments showed that a greater number of points were unnecessary for the present purpose, and also that the technique employed gave a curve with negligible hysteresis loop.

The data were treated as follows. For each measurement the percentage elongation was calculated from the measured lengths. This was divided into the corresponding load causing the elongation. The values of load divided by elongation were then plotted against elongation, and the resulting curve extrapolated to zero elongation. The resulting intercept was divided by the area of cross-section of the test-piece, and converted to Young's modulus at zero elongation in kg. per sq. cm. It is this value of modulus which is used throughout the subsequent discussion.

The density of each sample was calculated from the measured weight and dimensions. From the known ratio of weight of filler to weight of rubber plus curing agents (obtained on the raw mixes) and from the densities of the cured stocks, the volume loadings were calculated.

In order to obtain a reference for the state of cure of the samples, the T-50 test was performed on specimens cut from the cured strips.

The data obtained (density, volume loading, T-50, and Young's modulus) are collected in Table II. Figures following letter codes refer to times of cure, except for stock L. Here the first figure indicates mold cavity, the second, time of cure. Small letter (*a*) following the letter code indicates a repeat cure, made from the same mix.

## DISCUSSION OF RESULTS

Before proceeding to an analysis of the results, it is desirable to obtain some idea of the accuracy of these measurements. This may be obtained from the data for samples L-30 and L-45 (Table II). These are gum stocks, and were cured with the object of determining whether or not there is any difference in curing rate between the cavities 1, 3, and 5 of the mould. The fact that the two sets of three measurements agree among themselves shows that the curing does not depend on the cavity of the mold. The maximum variation within each of these sets of three measurements is about 1 per cent. It is believed that the individual measurements of Young's modulus, listed in Table IV, all have about this same accuracy.

Comparison of stocks S and W, however, shows that variations in modulus of 4 to 5 per cent may occur as a result of different curing conditions. These two stocks were prepared from the same mix, but cured on different days. Variations of this type were not controlled in these experiments: They therefore represent the limit of accuracy of the absolute values recorded. It seems reasonable, however, to expect relative accuracy greater than this when comparing samples cured in the same load.

TABLE II

	Density of cured strip	Volume percentage of filler 100%	Minus <i>T</i> -50 of cured strip	Percentage Elongation in <i>T</i> -50 test	Young's modulus at zero elongation (kg. per sq. cm.)
<i>Gum stocks</i>					
<i>SLS</i> 45	0.928	—	10.8	800	9.48
60	0.930	—	15.2	800	(9.08)
75	0.930	—	18.9	800	9.64
<i>SMN</i> 45	0.940	—	12.8	800	13.76
60	0.941	—	16.1	800	13.10
75	0.940	—	17.7	800	12.43
90	0.941	—	20.1	800	12.99
<i>SMN(a)</i> 45	—	—	17.3	800	13.06
60	—	—	19.8	800	12.78
75	—	—	22.1	800	12.87
90	—	—	24.6	800	12.28
<i>L-1</i> 30	0.982	—	-0.5	800	12.72
<i>L-3</i> 30	0.987	—	0.9	800	12.56
<i>L-5</i> 30	0.982	—	-0.3	800	12.56
<i>L-1</i> 45	0.983	—	10.0	800	14.28
<i>L-3</i> 45	0.986	—	9.8	800	14.17
<i>L-5</i> 45	0.989	—	8.9	800	14.22
<i>S</i> -45	0.973	—	10.2	800	13.61
60	0.972	—	13.8	800	13.97
75	0.984	—	16.2	800	13.59
90	0.987	—	19.5	800	13.02
<i>W</i> 45	0.984	—	11.8	800	14.28
60	0.988	—	15.3	800	14.40
75	0.979	—	18.8	800	13.61
90	0.984	—	21.3	800	12.85
<i>Carbon black</i>					
<i>O</i> 45	1.024	6.4	12.8	350	18.32
60	1.023	6.4	16.9	350	18.93
60	1.031	6.4	17.5	350	17.57
75	1.030	6.4	<i>B</i>	350	(16.92)
90	1.037	6.4	29.7	350	16.83
<i>SMP</i> 45	1.015	9.6	5.3	350	19.56
60	1.017	9.6	12.6	350	19.70
75	1.018	9.6	15.0	350	19.70
90	1.018	9.6	17.2	350	19.10
<i>SMP(a)</i> 45	—	9.6	—	350	20.7
60	—	9.6	—	350	21.4
75	—	9.6	—	350	19.87
90	—	9.6	—	350	18.91
<i>N</i> 45	1.109	23.5	5.1	350	44.1
60	1.111	23.5	9.8	350	44.5
60	1.108	23.5	7.2	350	42.1
75	1.110	23.5	15.8	350	(36.0)
90	1.116	23.5	17.2	350	42.7
<i>P</i> -33					
<i>P</i> 45	1.068	10.1	9.8	500%	17.37
60	1.077	10.1	15.9	500	17.52
60	1.063	10.1	16.8	500	17.18
75	1.070	10.1	25.1	500	(15.52)
90	1.069	10.1	21.9	500	16.00

TABLE II.—*Continued*

	Density of cured strip	Volume percentage of filler 100%	Minus T-50 of cured strip	Percentage Elongation in T-50 test	Young's modulus at zero elongation (kg. per sq. cm.)
<i>Thermax black</i>					
SMO 45	1.022	9.0	12.3	650	15.92
60	1.023	9.0	17.4	650	15.39
75	1.022	9.0	19.6	650	15.01
90	1.023	9.0	22.7	650	14.78
<i>SMO(a)</i>					
45	—	9.0	10.6	650	16.22
60	—	9.0	16.2	650	15.27
75	—	9.0	19.1	650	15.21
90	—	9.0	23.0	650	14.50
<i>Kadox zinc oxide</i>					
X 45	1.191	5.9	11.3	500%	18.08
60	1.197	5.9	17.8	500	19.42
75	1.188	5.9	22.1	500	19.73
90	1.191	5.9	25.6	500	20.2
<i>Y</i>					
45	1.417	10.6	9.4	500	21.5
60	1.420	10.6	14.5	500	22.9
75	1.410	10.6	19.3	500	24.0
90	1.415	10.6	23.2	500	25.7
<i>XX zinc oxide</i>					
Z 45	1.211	5.4	4.2	500%	16.91
60	1.197	5.4	9.9	500	18.43
75	1.193	5.4	14.8	500	19.48
90	1.197	5.4	19.3	500	19.67
<i>AA</i>					
45	1.413	10.4	1.9	500	20.4
60	1.409	10.4	7.2	500	22.1
75	1.410	10.4	11.6	500	23.4
90	1.419	10.4	16.2	500	24.9
<i>AB</i>					
45	1.873	20.9	-1.5	500	28.4
60	1.872	20.9	3.6	500	30.2
75	1.865	20.9	7.2	500	32.1
90	1.872	20.9	12.0	500	34.1
<i>Gilders' whitening</i>					
SLT 45	1.001	4.1	13.2	650	10.29
<i>T</i>					
45	1.067	3.8	9.8	650	16.42
60	1.078	3.8	16.7	650	16.55
75	1.063	3.8	18.9	650	15.95
90	1.069	3.8	20.1	650	15.37
<i>SLU</i>					
60	1.072	8.3	15.4	500	11.77
75	1.071	8.3	16.4	500	11.97
<i>U</i>					
45	1.141	10.3	9.1	500	18.68
60	1.134	10.3	17.2	500	18.62
75	1.137	10.3	21.2	500	18.50
90	1.144	10.3	23.0	500	17.93
<i>V</i>					
45	1.295	20.6	6.3	500	24.8
60	1.301	20.6	15.4	500	25.1
75	1.300	20.6	17.6	500	24.9
90	1.298	20.6	20.5	500	23.2
<i>Catalpo clay</i>					
R 45	1.118	10.4	-2.8	500	19.37
60	1.113	10.4	5.4	500	21.25
75	1.128	10.4	11.5	500	21.15
90	1.126	10.4	17.0	500	21.7

Data in parentheses were omitted when considering the results. The 60-minute cure of SLS and the 75-minute cure of N, O, and P gave discordant moduli, possibly because of irregular curing conditions.

It is necessary to know the modulus of the matrix in the compounded stocks, to check the theoretical result contained in Equation (12). It was intended to measure the moduli for each mix over a range of cures, and plot these values against the corresponding T-50. It should then be a legitimate procedure to assume that the modulus of the matrix in the compounded stock, for a particular point of the modulus-T-50 curve, is equal to the modulus of the gum stock at the corresponding point of its modulus-T-50 curve. This procedure proved to be impracticable for the following reasons.

Because of the varying characteristics of the compounds studied, it was not possible to obtain significant T-50 values at a single elongation. Reference to Table II shows that the elongations varied from 350 per cent for the highly loaded stocks, to 800 per cent for the gum stocks. It seems unlikely that the T-50 values are comparable throughout this wide range of elongation.

A more serious factor in precluding the use of T-50 as a reference for state of cure lies in the fact that the modulus-T-50 curves differed greatly in shape, depending on the filler used. The gum stocks showed a fairly pronounced maximum. The carbon black stock, however, was nearly flat throughout a large part of the curve, and the compound containing Kadox zinc oxide showed a steadily increasing modulus with decreasing T-50. Obviously it is impossible to pick from these curves any satisfactory reference point.

Another difficulty lies in the fact that two different curves were obtained for stocks *S* and *W*. These were made from the same mix, but cured on different days. The fact that the differences in modulus shown by these two stocks are not reflected in the T-50 test means that some other factor enters into the results.

In default of any better procedure, it was decided to assume arbitrarily that the modulus in the compounded stock is equal to the modulus of the gum stock which had the same curing time. Whenever a gum stock was included in the press load its modulus was used in calculating the relative modulus ( $M^*/M$ ). In those cases in which no gum stock was in the mold, the average for stocks *S* and *W* was set equal to  $M$ , the modulus of the matrix, for stocks *N* to *AB*.

This procedure is arbitrary and in some cases definitely wrong—for example, the stocks containing zinc oxide. However, the conclusions to be drawn from the data do not depend upon this method of calculation, but would follow from any of a number of other methods which have been employed.

The values so obtained are summarized in Table III, together with the average relative modulus for all cures of each mix, and the calculated value of this quantity. Relative moduli, averaged over all cures, are plotted against  $\Phi$  in Figure 1. Examination of these data shows that in no case (with the exception of Kadox and XX zinc oxide) is there any pronounced variation in relative modulus as cure progresses. This may be taken as justification of the validity of the procedure employed, for fillers other than zinc oxide.

It is at once evident that there are many discrepancies between the observed and calculated values. To obtain information from these measurements, it is desirable to examine each filler separately.

#### CARBON BLACK

The values observed for relative modulus are markedly greater than the calculated values. To account for these discrepancies it is only necessary to recall that carbon black is generally recognized to be flocculated in rubber<sup>6</sup>. When flocculated, the filler particles are, on the average, much closer together than would be the case for perfect dispersion. It is therefore evident that the



TABLE III

Code	Filler	$M^*/M$					Observed average	Calculated
		100 $\Phi$	45 min.	60 min.	75 min.	90 min.		
$\left. \begin{matrix} O \\ SMP \\ SMP(a) \\ N \end{matrix} \right\}$	Carbon black	6.4	1.31	1.34	1.25	1.30	1.30	1.16
		9.6	1.42	1.50	1.58	1.47	1.54	1.24
		9.6	1.59	1.68	1.54	1.54	1.54	1.24
		23.5	3.16	3.14	2.97	3.30	3.17	1.59
P	P-33 black	10.1	1.25	1.24	1.21	1.24	1.24	1.25
$\left. \begin{matrix} SMO \\ SMO(a) \end{matrix} \right\}$	Thermax black	9.0	1.16	1.17	1.21	1.14	1.19	1.22
		9.0	1.24	1.20	1.18	1.18	1.18	1.22
$\left. \begin{matrix} X \\ Y \end{matrix} \right\}$	Kadox zinc oxide	5.9	1.27	1.35	1.45	1.57	1.41	1.15
		10.6	1.51	1.59	1.76	2.00	1.72	1.26
$\left. \begin{matrix} Z \\ AA \\ AB \end{matrix} \right\}$	XX zinc oxide	5.4	1.21	1.30	1.43	1.52	1.37	1.13
		10.4	1.47	1.56	1.72	1.92	1.68	1.26
		20.9	2.04	2.13	2.36	2.64	2.29	1.52
$\left. \begin{matrix} SLT \\ T \\ SLU \\ U \\ V \end{matrix} \right\}$	Gilders' whitening	4.1	1.09	—	—	—	1.09	1.10
		3.8	1.18	1.17	1.17	1.19	1.18	1.09
		8.3	—	1.23	1.24	—	1.24	1.21
		10.3	1.34	1.31	1.36	1.39	1.35	1.26
		20.6	1.78	1.77	1.83	1.79	1.79	1.51
R	Catalpo clay	10.4	1.42	1.52	1.56	1.67	1.54	1.26

assumptions underlying Equation (12) are not fulfilled. Thus, if the carbon particles are far apart from each other within the rubber, their effects on the displacement when the rubber is stretched will be additive. If, however, the particles are close together, their effects on the displacement in the rubber will be far from additive. It is physically obvious that, when the particles are near together, the increase in modulus is greater than when they are far apart. Suppose, for example, that all of the particles in a dilute mix were placed touching each other, and in lines parallel to the direction of stretch. Assuming complete adhesion and rigid particles, it is evident that the overall structure would also be rigid, the effect of the contacting particles being similar to a rigid bar immersed in the elastic rubber. Another factor that may be of

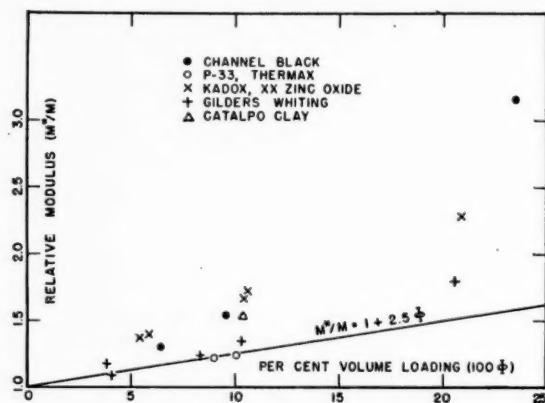


FIG. 1

importance is our neglect of the molecular structure of the rubber, since the carbon black particle is not large compared to this structure.

## SOFT BLACKS (P-33, THERMAX)

These fillers yield values for relative modulus substantially in agreement with those calculated from Equation (12). It appears that soft blacks are well dispersed in rubber, and that, at small elongations, there is good adhesion between the matrix and the filler.

## ZINC OXIDES (KADOX AND XX ZINC OXIDE)

These fillers did not show conformity to Equation (12) according to these experiments. Microscopic studies have shown that zinc oxide is well dispersed in rubber. The relative moduli, however, are abnormally high. Because of the microscopic evidence this cannot be ascribed to flocculation of the filler. It may be in part owing to the acicular shape of the ultimate particles of zinc oxide (see Catalpo clay, below), but this cannot account for the entire effect produced. It is also noteworthy that these stocks do not show any reversion, *i.e.*, decrease in modulus in the longer cures, throughout the range of cures employed in these experiments. This behavior is distinct from all other samples studied in this series. It seems fair to assume that the abnormalities in modulus shown by zinc oxide are caused by the effect of this filler on the type of cure of the rubber matrix, and we may conclude from the present results that the high modulus of zinc oxide stocks is attributable to a pronounced stiffening of the rubber matrix, but that in other respects the filler is normal and well dispersed. This interpretation requires the assumption that in the most extreme case (stock AB, 90 minute cure, 20 per cent by volume XX zinc oxide) the modulus of the matrix is 50-60 per cent greater than that of the pure gum blank. This does not seem improbable.

## WHITING

The relative moduli of tetramethylthiuram sulfide stocks are in complete agreement with the calculations, but the relative moduli of the mercaptobenzothiazole stocks are higher than the calculated values by an amount which appears to be greater than the experimental error. The cause of this discrepancy is not known. It should be pointed out that at volume loadings as high as 20 per cent discrepancies may be expected to occur, since at these concentrations the suspension can no longer be considered dilute. It may be concluded that whiting is well dispersed in rubber.

## CATALPO CLAY

The relative modulus is abnormally high. This behavior is undoubtedly to be interpreted as being caused by the pronounced acicular shape of the clay particles. The strips on which Young's moduli were determined were made from a calendered stock, and the direction of stretch coincided with that of the calender grain. It is well known that calendering a stock containing an anisotropic filler results in alignment of the filler particles in the direction of the calender grain. Because of this, the effective volume loading is greater in this direction than that calculated on the assumption of spherical particles<sup>7</sup>. The increase in modulus is, therefore, greater than expected. Other measure-

ments on Catalpo clay stocks in which there was little if any calender grain have shown agreement with Equation (12).

In conclusion it can be stated that Equation (12) gives a satisfactory representation of the increase in modulus of a rubber compound due to addition of a filler whenever certain idealized conditions are approximately fulfilled. These conditions are caused by the simplifying assumptions made in carrying out the calculations. According to these assumptions, the filler particles must be spherical, or nearly so, and there must be complete adhesion between the rubber and the filler. The filler is assumed to be completely and uniformly dispersed, and at a volume loading small enough to justify neglect of effects due to pairs of particles. Throughout the calculations the rubber matrix has been treated as a continuous medium. It is possible that extremely small filler particles might require consideration of the molecular structure of the rubber hydrocarbon.

Equation (12) is thus an idealized limiting law. As illustrated in the discussion of the experimental results presented here, departures from this law may lead to conclusions on the dispersion of the filler and on the state of vulcanization of the rubber matrix.

Dependence of reinforcement on particle size of filler is worthy of further discussion. Throughout the majority of the literature on the subject, it has been assumed that decreasing particle size means increasing reinforcement. The calculations reported in this paper show that, in the ideal case, there can be no primary relation between the particle size of filler and reinforcement, judged by modulus at low elongations. Experiments other than those reported here show that carbon black gives greater increases in modulus than other commercial fillers and that, for a given volume loading and time of vulcanization, substantially all other commercial fillers show much the same modulus at low elongations. Cotton<sup>8</sup> and others have prepared sheets of rubber containing rigid inclusions several millimeters in diameter. These inclusions cause approximately the same increase in modulus, as do fillers with particle diameter of the order of 1 micron. This similarity between microscopic particles and rigid inclusions some 1000-10,000 times larger is, of course, in agreement with Equation (12). If there were any functional dependence of reinforcement on particle size, it could only become evident at particle sizes well under 1 micron. It appears, therefore, that theory and experiment agree in the conclusion that there is no direct relationship between reinforcement and particle size of filler.

It is entirely possible, however, that particle size of filler may affect indirectly the phenomena of reinforcement. This can occur through either of two mechanisms. Fillers which tend to flocculate in rubber may do so to a greater or less extent. The extent of flocculation may be determined in part by the particle size of the filler. Alternatively, some fillers affect the state of vulcanization or the type of cure of the rubber matrix. The magnitude of these effects may well depend on the particle size of such fillers. In addition, as noted above, when the particle size becomes so small that the rubber can be treated no longer as a continuum, other effects may require attention. These effects might appear whenever particle size is of the same order of magnitude as, or smaller than, the molecular dimensions of the rubber.

#### SUMMARY

1. Analysis shows that, subject to certain limitations, the modulus of a loaded stock ( $M^*$ ) depends on the modulus of the rubber matrix ( $M$ ), accord-

ing to the equation:

$$M^* = M(1 + 2.5\Phi)$$

where  $100\Phi$  is the volume percentage of filler.

When these limitations are fulfilled, the effect of compounding on modulus is, therefore, independent of the particle size of the filler.

The assumptions on which this equation is founded are as follows: (1) the filler particles are spherical; (2) there is complete adhesion between rubber and filler; (3) the elongation is small; (4) the filler is completely dispersed; (5) the volume loading is small; (6) the filler particles are sufficiently large that the molecular structure of the rubber may be neglected.

2. The stresses about a filler particle have been derived mathematically.

3. Experimental data check the calculations for the following fillers: P-33, Thermax, and whiting. Catalpo clay presents some anomalies because of its acicular particles.

4. Carbon black does not conform to the calculations. This is attributed to the fact that it is strongly flocculated in rubber.

5. Zinc oxide (Kadox or XX zinc oxide), which should conform, because it is well dispersed in rubber, causes abnormally large increases in modulus, presumably because of alteration of the type of cure and consequent alteration of the modulus of the rubber matrix.

#### ACKNOWLEDGMENT

It is a pleasure to express my indebtedness to M. Mooney of these laboratories for his continued interest and helpful advice in carrying out the calculations reported in this paper.

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# THE VARIATION WITH TEMPERATURE OF THE DYNAMIC PROPERTIES OF RUBBER AND SYNTHETIC RUBBERLIKE MATERIALS\*

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## INTRODUCTION

The development during the last twenty years of reliable methods for the bonding of rubber to metal<sup>1</sup> has led to a vast increase in the use of rubber for the purpose of vibration insulation and damping. It has been found that the elastic moduli of rubber derived from static stress-strain measurements differ considerably from the values obtained from dynamic experiments. Discussions on this point<sup>2</sup> have figured prominently in the literature of recent years. The growing interest in the dynamic properties of rubber is due largely to the demand for reliable figures from which to design and calculate the efficiency of antivibration mountings and vibration dampers, and consequently numerous methods<sup>3</sup> have been developed for the investigation of these properties. The apparatus to be described has been in use for some time for such work and for routine testing of rubber samples. Recent work<sup>4</sup> has suggested that dynamic measurements may be used with advantage in the investigation of the more academic problems regarding the nature of the rubberlike state.

In the course of experiments to determine the dynamic properties of certain butadiene-styrene copolymer (Buna-S) compounds, considerable variation was encountered, and this appeared to depend largely on the temperature of the material under test. Some information on such temperature effects may be found in the literature<sup>5</sup>. It appeared, however, that an investigation of these effects in the region of normally occurring temperatures (0°–40° C) would give results having considerable importance in view of the present necessity for large-scale conversion to synthetic rubbers for the manufacture of antivibration equipment. The behavior of these materials at temperatures below 0° C is of course of great significance to the aircraft industry, but such measurements were outside the scope of available apparatus and are to be made the subject of a later investigation.

## APPARATUS

The test-pieces used were moulded cylinders of  $\frac{7}{8}$  inch length and  $\frac{3}{4}$  inch diameter, bonded at each end by the brass-plate process to a steel screw having a flat face of diameter equal to that of the rubber (Figure 1). The base of the apparatus, the general scheme of which is shown in Figure 2, consisted of a massive cast iron block mounted on four rubber mountings, chosen to give the block a natural frequency sufficiently low to provide adequate vibration insulation from the surroundings, and also to prevent absorption by the base of appreciable energy from the vibrator described below. Four test-pieces of the type detailed above, and arranged symmetrically, supported from the block a

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rigid angle iron frame which formed the vibrating member. Bolted to this frame was a  $\frac{1}{8}$  h.p. variable speed electric motor, the spindle of which carried a threaded cross-piece. Small masses having tapped holes could be screwed on to this cross-piece to provide a variable amount of unbalance to the rotating system. The join of the cross-piece and the spindle was arranged to be at the centre point which was also the centre of gravity of the whole suspended system, so that the vibrating force exerted on driving the motor should be divided equally among the four test pieces. The motor was connected by a flexible coupling to the generator of an electric tachometer, and this generator also

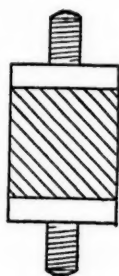


FIG. 1.—Diagram of test-piece.

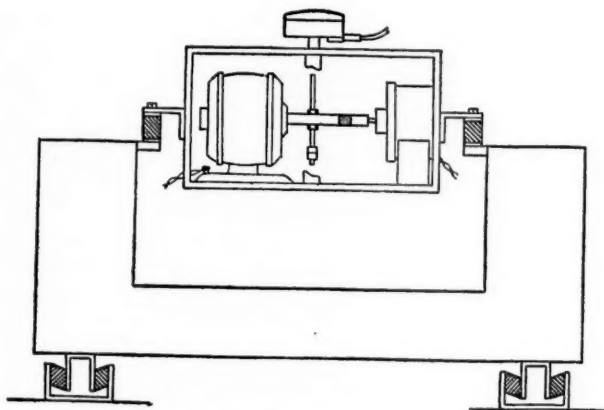


FIG. 2.—Diagram of machine.

served to balance the weight of the motor about the centre point of the frame. The tachometer indicator, mounted externally, was wired to the generator by flexible leads.

The vibration of the frame was detected by an inertia type piezo electric pick-up (delivering an e.m.f. proportional to the instantaneous acceleration) bolted rigidly to its upper member and wired to a vibration meter<sup>6</sup> (supplied by the General Radio Co. of America). This instrument consists of a double integrating amplifier, *i.e.*, one having amplification inversely proportional to the square of the frequency of the input signal, to compensate for the pick-up characteristic and deliver a voltage proportional to the amplitude of the vibration and independent of frequency. The meter on this instrument was cali-



brated directly with the pick-up to indicate R.M.S. vibration amplitude within a range (covered by means of a 10 position multiplier switch operating a stepped attenuator) of  $2 \times 10^{-5}$  to 3 inches and this calibration was corrected throughout the temperature range as described below. The wave-form of the double integrated signal from the vibration meter was observed on a cathode-ray oscillograph to ensure that a pure harmonic motion was obtained. Brief mention of this part of the apparatus has been made in a previous paper<sup>7</sup>.

A stout wooden box enclosed the whole of the apparatus, and the enclosure was either heated by means of four 32 candle-power carbon-filament lamps carrying a controlled current, or cooled by solid carbon dioxide contained in two wire baskets at the ends of the chamber. Three copper-constantan thermojunctions supported in the air in close proximity to three of the test-pieces, and a fourth junction embedded in the block at a point close to the remaining test piece, were wired to a sensitive galvanometer and after calibration against an accurate mercury thermometer, served to measure the corresponding temperatures. The enclosure was brought to a uniform temperature by means of air circulation induced by a small electric fan affixed to one end of the box. The temperatures denoted by the four thermocouples differed by less than  $1^\circ \text{C}$  at the times when measurements were made.

The equipment is similar to that used by Gehman<sup>8</sup> for measurements on rubber mountings. The use of two contrarotating eccentric mass systems by Gehman gave a resultant vertical vibrating force, the horizontal components being equal and  $180^\circ \text{C}$  out of phase. It was not considered necessary to utilize this device in the present work, since the crystal pick-up was very insensitive to horizontal movement and, in addition, all measurements were made in the condition of resonance for the vertical component of vibration, the corresponding frequency was far removed from the frequency for horizontal resonance owing to the low ratio of shear stiffness to compression stiffness of the system of mountings, and hence the horizontal amplitude was negligible.

### THEORY

To investigate the motion of systems similar to that described above previous workers have postulated an equation of the form:

$$M \frac{d^2x}{dt^2} + B \frac{dx}{dt} + Sx = F \sin pt \quad (1)$$

where  $M$  represents the mass of the suspended system,  $x$  its instantaneous vertical displacement from the equilibrium position,  $B$  the constant of proportionality between velocity and force having the nature of viscosity,  $S$  the spring rate of the mounting system,  $F$  the amplitude of applied force,  $p$  its angular frequency, and  $t$  the elapsed time, all quantities being measured in c.g.s. units. It is evident in the present case that the force amplitude is not invariant with frequency and is in fact expressed by the equation:

$$F = p^2 \Sigma mr \quad (2)$$

where  $\Sigma mr$  represents the sum of the products of out-of-balance masses and their respective distances from the axis of rotation. Equation (1) is thus transformed to:

$$M \frac{d^2x}{dt^2} + B \frac{dx}{dt} + Sx = (p^2 \Sigma mr) \sin pt \quad (3)$$

This equation is of familiar form, and its solution when steady vibration has set in is:

$$x = \frac{(p^2 \Sigma mr) \sin(pt - \alpha)}{\{(S - Mp^2)^2 + B^2 p^2\}^{1/2}}, \quad \alpha = \tan^{-1} \frac{Bp}{S - Mp^2} \quad (4)$$

If  $p$  is varied and  $S$  and  $M$  maintained constant, maximum amplitude occurs when  $p^2 = 2S^2/(2MS - B^2)$ , but in all practical cases  $B^2 \ll 2MS$  and may be neglected, giving as condition for maximum amplitude:

$$p_c^2 = S/M \quad (5)$$

the amplitude being

$$X_m = p_c \Sigma mr / B \quad (6)$$

The spring rate,  $S$ , of the system of four mountings may be expressed in terms of the dynamic compression modulus of elasticity of the rubber, using the conventional laws of elasticity:

$$S = 4EA/L$$

$E$  representing the modulus<sup>9</sup> of the rubber, and  $A$  and  $L$  the cross-sectional area and length respectively of each mounting. Using Equation (5), the modulus may be expressed in terms of measurable quantities, *i.e.*:

$$E = p_c^2 ML / 4A, \quad E = \pi^2 \nu_c^2 ML / A \quad (7)$$

where  $\nu_c = p_c / 2\pi$  is the actual frequency for maximum amplitude of vibration. This is known as the resonant frequency, since, as shown below, it is equal to the natural frequency of vibration of the system.

If the system were given a vertical displacement and then allowed to vibrate freely, the motion would be described by equating the left-hand side of (1) to zero.

The solution of such an equation is well known:

$$x = (X \sin p_n t) \exp(-Bt/2M) \quad (8)$$

$X$  being the initial displacement and  $p_n = (S/M)^{1/2}$ .

The system thus executes a damped vibration of angular frequency equal to that leading to maximum amplitude for the case of forced vibrations ( $p_c$ , Equation (5)).

The damping of free vibrations expressed quantitatively is a convenient factor for expressing the losses occurring in rubber undergoing vibrational strain, and it is usual to define a quantity called dynamic resilience for this purpose. The definition of resilience has been made in various ways by different authors (a discussion on this point has been published<sup>10</sup>); in the present work resilience  $R$  is defined as the ratio, expressed as a percentage, of a wave amplitude to that immediately preceding it in a train of damped vibrations. Thus:

$$R = 100 \exp(-\pi B / Mp_n) \quad (9)$$

The resilience may be evaluated from the results of forced vibration experiments, using Equation (6):

$$R = 100 \exp(-\pi \Sigma mr / MX_m) \quad (10)$$

#### EXPERIMENTAL METHOD

The values of the dynamic moduli of certain types of rubberlike compound have been shown to depend on the vibration amplitude at which the measure-

ments were made<sup>11</sup>. Although this fact is of considerable interest, it was not desired to investigate it in the present experiments, and to avoid any variation on this account all measurements on any one set of test-pieces were made at a fixed value of resonant amplitude.

Similar observations have been made regarding the effect of static load (in this case due to the weight of the suspended system), and this load also was maintained constant during measurements upon each set of samples.

To correct for variation with temperature of pick-up sensitivity, the system was mounted on four helical steel springs, and the motor driven at a frequency considerably higher than the resonant frequency of the system. The unbalanced masses were adjusted to give an amplitude of the same order as that at which measurements were to be made. The indicated value of amplitude was then plotted against temperature throughout the temperature range of the experiment. The only factors which may cause variation in the actual amplitude are:

(a) Variation in eccentricity of the rotating masses due to thermal expansion or contraction. Over the whole range of temperatures, calculation shows this to be about 0.05 per cent.

(b) Variation on the stiffness of the steel springs. The maximum variation here is less than 2 per cent, but in addition, under the condition of this calibration (speed > resonant speed), reference to Equation (4) shows that amplitude is insensitive to slight variation in stiffness.

(c) Variation in hysteresis losses with temperature. For steel springs these are so small that their variation will have no appreciable effect.

The pick-up showed maximum response at 27.5° C, and readings of the vibration meter at this temperature were found by direct observation with a graduated microscope to be correct to within 5 per cent. The correction curve was, therefore, drawn up assuming correct calibration at 27.5° C, and there is thus the possibility of a constant percentage error in amplitude readings of not more than 5 per cent. This fact is not considered of first importance, since in the present experiments it would not affect the nature of the resilience temperature curves, but only their absolute levels.

The temperature having been stabilized at the required level by the methods previously described, the motor was started and accelerated up to the speed at which the amplitude reached a maximum value. If this value did not correspond to that previously decided upon, the position of the unbalanced masses was varied in the required direction and the procedure repeated. By means of two or three adjustments, resonance at the desired amplitude was obtained and the frequency was noted; the positions and values of the unbalanced masses were also noted, the mass of the suspended system was known as also were the dimensions of the test-pieces and hence all information for calculation of modulus (Equation (7)) and resilience (Equation (10)) was determined.

## RESULTS

Experiments have been carried out on natural rubber and a number of commercial synthetic rubberlike materials, some of known and some of undisclosed composition. In all cases the materials have been compounded (see Appendix) only with sufficient ingredients for the development of the elastic properties of the base material on vulcanization for 30 minutes at 153° C. Work on compounds reinforced by carbon black or other materials has been carried out and will be made the subject of a further paper. A pre-

liminary note<sup>12</sup> showing relative modulus-temperature relationships for a number of commercial natural rubber, GR-S (Buna-S) and Neoprene-E compounds has been published elsewhere. The relationships discussed in the present paper should be considered as properties of the raw materials available to the rubber industry, and in some cases at least the properties of the various synthetics may be made to approach those of natural rubber more closely by suitable compounding. As stated above, compounds were vulcanized for 30 minutes at 153° C, but in all cases it was established by experiment that little change was caused in the effects to be discussed by vulcanization for 45 or 60 minutes at 153° C.

*Modulus.*—In the present investigation the chief aim has been to evaluate the various materials in order of the temperature sensitivities of their moduli; the modulus values at 20° C are given in the Appendix, but in general the modulus results are presented in the form of curves of relative modulus against temperature, relative modulus at any temperature being defined as modulus at that temperature divided by modulus at 20° C. It will be seen from the theory of the method that the frequency at which any test is made is determined by the modulus of the rubber, and hence any variation of modulus due to temperature effects will vary the frequency of the test on any one material. This gives rise to the question of the dependence of modulus on vibration frequency, since in this work any variation on this account would be inseparable from the temperature effect. Evidence has been published<sup>13</sup> showing that in the frequency range of the present experiments (20–60 cycles per second) modulus is sensibly independent of frequency.

Except where otherwise stated tests were made with a static stress of 486 g. per sq. cm. superimposed on a dynamic strain amplitude of 0.65 per cent.

Reference to Figure 3 shows that of all the materials studied, natural rubber (curve A) was the least temperature-sensitive. The coefficient of decrease of modulus was  $2.7 \times 10^{-3}$  per ° C in the linear part of the curve from 5° to 30° C, falling to even smaller values at higher temperatures. Neoprene-GN, curve B, one of the early commercial synthetic rubbers, manufactured by polymerization of chloroprene, is 3 to 4 times as temperature-sensitive as natural rubber, although the shape of the curve does not permit the calculation of a temperature coefficient over any reasonable temperature range. Of particular interest is curve D for butadiene-styrene copolymer (Buna-S), which is the material chosen for large-scale replacement of natural rubber in automobile tires, and most mechanical rubber products. The modulus-temperature coefficient for Buna-S is about 5 times that of natural rubber in the range of temperatures employed in this investigation, and this fact should be taken into account in products where the modulus value is critical. Curve C (Figure 3) refers to Neoprene-YD, a material of similar chemical composition to Neoprene-GN. A number of measurements were also made on Neoprene-E, a widely used synthetic rubber of the same general type, but all the earlier results on this material were to some extent vitiated by a slow but progressive variation of its properties in the lower half of the temperature range. This effect is to be the subject of a more detailed investigation, but it would appear from the experiments so far made that some form of combined slow freezing and modulus-temperature hysteresis effect is exhibited by this material. The general trend of modulus values for Neoprene-E, as shown in the note<sup>12</sup> mentioned above, indicates a higher temperature coefficient than any illustrated in Figure 3.

The properties of Neoprene-Z (curve E, Figure 4) differ considerably from those of the other Neoprenes in that the material exhibits a much greater rela-

tive modulus variation; it should be noted that the scale of Figure 4 is one-fifth that of Figure 3. This high variation is no doubt bound up with the constitution of Neoprene-Z which is a copolymer of chloroprene with a second undisclosed component. The remaining curves of Figure 4 show the modulus-temperature relationships for a number of copolymers of butadiene and acrylonitrile in various proportions. Curves *F*, *G*, *H*, *I*, and *J* refer respectively to polymers with the following proportions of acrylonitrile to butadiene: 45-55 (Hycar OR-15), 35-65 (Buna-N type 35/65), 35-65 (Hycar OR-25), 25-75

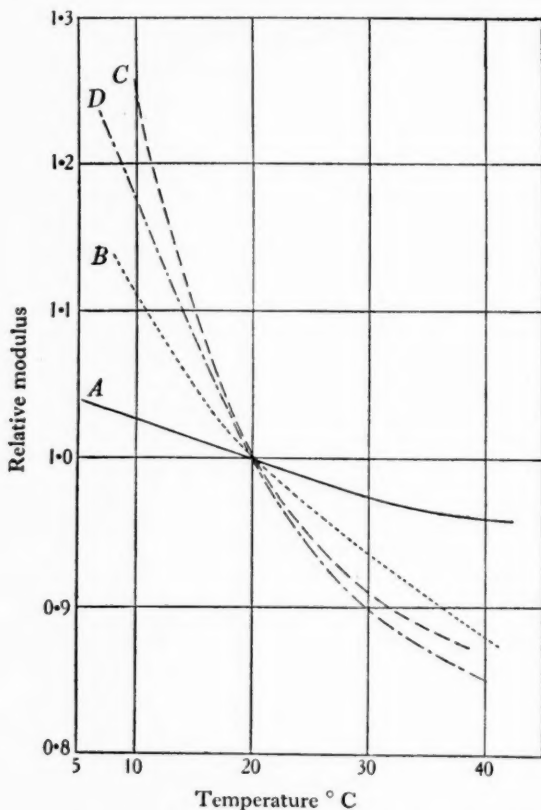


Fig. 3.—Curves of relative modulus against temperature for natural rubber (*A*), Neoprene-GN (*B*), Neoprene-YD (*C*), Buna-S (*D*).

(Buna-N type 25/75), 25-75 (Perbunan). It will be observed that increasing concentration of acrylonitrile increases the temperature sensitivity of the polymer. The relationship of modulus to temperature for Hycar OR-15, curve *F*, seems best represented by two straight lines intersecting at 20.2° C. On the low-temperature side the coefficient of modulus decrease with temperature is  $1.3 \times 10^{-1}$  per °C, and on the high-temperature side  $0.14 \times 10^{-1}$  per °C. Curves *G* and *H* show that polymers of the same chemical composition but produced by different manufacturers have the same modulus-temperature relationship above 20° C, but that a deviation occurs at lower tempera-

tures. Curves *I* and *J* show similar effects for two types of 25 acrylonitrile-75 butadiene copolymer made in this instance by the same manufacturer.

The curve shown on the top right of Figure 4 is of actual modulus against temperature for Thiokol-RD, a mixed polymer of undisclosed composition. It is not possible to construct a curve of relative modulus (referred to 20° C) against temperature for this material, since the modulus increases very sharply as temperature decreases towards 20° C, and the value at that temperature is outside the range of the equipment. In this case it was necessary to use a static load of 812 g. per sq. cm. and make measurements at a resonant amplitude corresponding to 0.325 per cent strain.

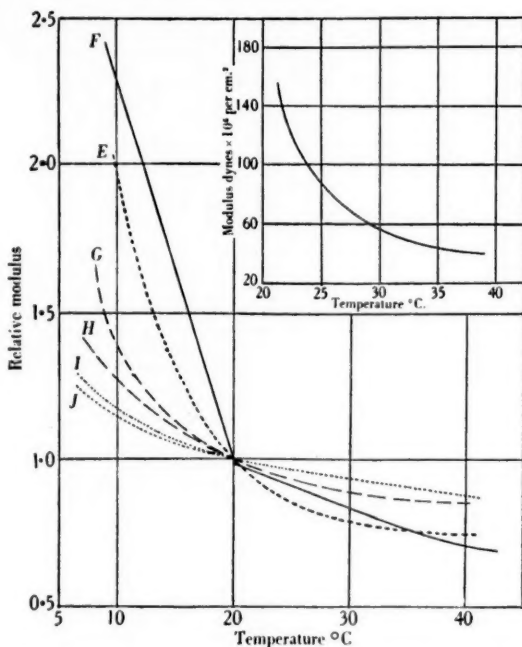


FIG. 4.—Curves of relative modulus against temperature for Neoprene-Z (*E*), Hycar OR-15 (*F*), Buna-N 35/65 (*G*), Hycar OR-25 (*H*), Buna-N 25/75 (*I*), Perbunan (*J*). Inset, curve of modulus against temperature for Thiokol-RD.

One factor which applies to all relative modulus-temperature curves to a greater or lesser degree is that the temperature coefficient of modulus is negative and decreases numerically with increasing temperatures.

**Resilience.**—As with the modulus measurements the variation of the test frequency throughout the range of temperatures employed is not considered to have any appreciable effect on the values obtained. Evidence of this view is provided by a number of workers<sup>13</sup>. In the case of each of the materials illustrated by Figure 5, the resilience-temperature relationship is composed of two straight lines; to indicate the average degree of scattering of results the experimental points are shown on curves *A* (natural rubber) and *E* (Neoprene-Z). The intersection of the component straight lines occurs at 22° to 22.5° C for natural rubber, Neoprene-GN (curve *B*), Neoprene-YD (curve *C*), and Buna-S (curve *D*) and at 30.5° C for Neoprene-Z. The curves for Neoprene-GN and



Buna-S are similar in shape to that for natural rubber although they lie at different levels; this demonstrates the overall superiority of natural rubber from the point of view of resilience. The fact that curve *E* for Neoprene-Z crosses those for all materials but natural rubber shows the importance of qualifying resilience figures by statement of the test temperature when comparing materials for resilience. The experiments on Neoprene-E were largely abortive for reasons similar to those given in the discussion of modulus results.

Figure 6 gives the resilience-temperature curves for the remaining materials; except in the case of Hycar OR-15 (curve *F*) the curves are not composed of two linear components with a sharp transition as were those shown on Figure 5. It is interesting to note that in the region 10° to 20° C the order of the compounds in increasing resilience corresponds to their order in decreasing relative

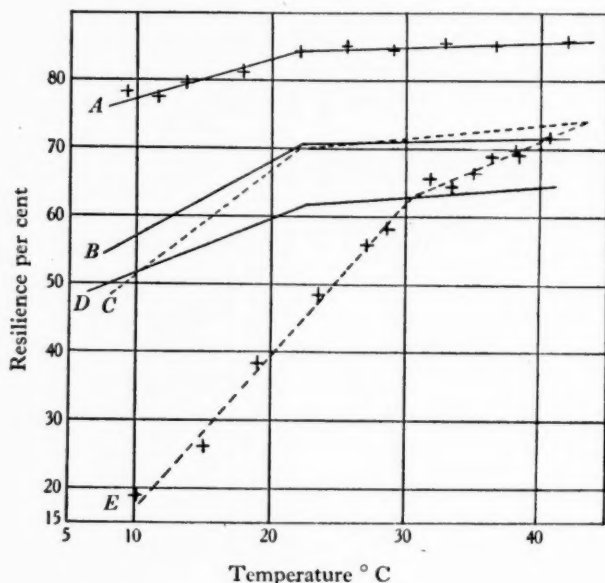


Fig. 5.—Curves of resilience against temperature for natural rubber (*A*), Neoprene-GN (*B*), Neoprene-YD (*C*), Buna-S (*D*), Neoprene-Z (*E*).

modulus on Figure 4. In the case of Hycar OR-25, Buna-N 25/75, and Perbunan fairly steady values of resilience are maintained from 30° C to the upper limit of temperature employed. Curve *K* for Thiokol-RD appears to have a minimum at 23.25° C at which temperature the modulus (Figure 4 inset) is rising very sharply with temperature decrease. The inference is that Thiokol-RD is tending to freeze at some temperature in the region 15°–20° C, giving values of modulus and resilience commonly associated with crystalline materials. Hycar OR-15 (curve *F*) gives a suggestion of a similar maximum at some lower temperature, and it is interesting to note that, using a pendulum rebound method of resilience measurement, Jones and Snyder<sup>14</sup> found a minimum for this material at about 11° C. A curve given by these workers for Perbunan is of the same general shape and level as that shown in Figure 6, curve *J*.

## CONCLUSIONS

(1) Over the range from 5° to 40° C, the temperature coefficients of the dynamic compression moduli of all the rubber and rubberlike materials studied are negative and fall numerically with increasing temperature.

(2) The highest numerical value of this coefficient for natural rubber is  $-2.7 \times 10^{-3}$  per °C. Neoprene-GN has a coefficient 3 to 4 times this value and Buna-S about 5 times. Hycar OR-15 shows the highest coefficient of  $-1.3 \times 10^{-1}$  per °C from 10 to 20° C, the value changing sharply at 20.2° C to  $-0.14 \times 10^{-1}$ , which is maintained up to 40° C.

(3) Results for Neoprene-E were not reproducible, owing to a type of slow freezing effect.

(4) In all cases but Thiokol-RD resilience tended to increase with increasing temperature throughout the range.

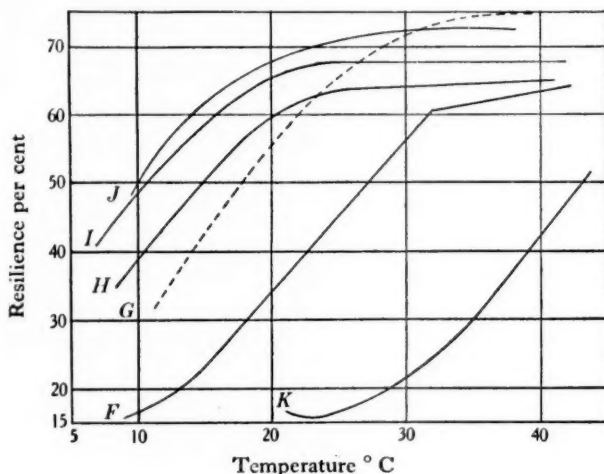


Fig. 6.—Curves of resilience against temperature for Hycar OR-15 (F), Buna-N 35/65 (G), Hycar OR-25 (H), Buna-N 25/75 (I), Perbunan (J), Thiokol-RD (K).

(5) Resilience-temperature curves for natural rubber, Neoprene-GN, Neoprene-YD, and Buna-S take the form of straight lines intersecting at 20° to 22.5° C. Neoprene-Z shows a similar effect with intersection at 30.5° C. and Hycar OR-15 similarly at 31.5° C.

(6) Copolymers of butadiene and acrylonitrile show increasing modulus-temperature coefficient, and in the region 10° to 20° C decreasing resilience with increasing acrylonitrile content. The resilience-temperature diagrams for these polymers, except Hycar OR-15, are smooth curves which appear to reach steady values towards the upper end of the temperature range.

(7) Thiokol-RD appears to have a freezing-point, under the dynamic conditions employed, somewhere in the region of 15–20° C; there is evidence that Hycar OR-15 shows a similar effect between 0° and 10° C.

(8) The relationships enumerated above refer to basic compounds of the various materials. How far the temperature effects may be reduced or modified by suitable compounding is the subject of continuing investigation.

## ACKNOWLEDGMENTS

This work forms part of a program of research into the properties of rubber-like materials for engineering applications being carried out in the laboratories of John Bull Rubber Co., Ltd., and Metalastik, Ltd., Leicester, to whom acknowledgment is made for permission to publish this paper. The authors desire to express their thanks to C. M. Blow for help and advice in planning this investigation.

## APPENDIX

(1) *Compounds*.—The following compounding formulas are by weight:

Natural rubber (smoked sheet)	100	Buna-S	100
Sulfur	3	Sulfur	3.75
Mercaptobenzothiazole	0.75	Mercaptobenzothiazole	1.0
Stearic acid	1.0	Iranolin RT-2228*	12.5
Zinc oxide	4	Mineral rubber	12.5
		Zinc oxide	6.25

\* High-boiling aromatic distillate.

Neoprene type	GN 100	YD 100	Z 100
Wood rosin	—	5	5
Calcined magnesia	4	10	10
Zinc oxide	1	10	5
Sulfur	—	1	1
Tricresyl phosphate	5	5	5
Cottonseed oil	5	5	5

General formula applying to Hycar OR-15, Hycar OR-25, Thiokol-RD, Perbunan, Buna-N 35/65, Buna-N 25/75:

Polymer	100
Zinc oxide	5
Santocure accelerator*	0.75
Sulfur	1.5
Tricresyl phosphate	20
Stearic acid	1.0

\* 2-cyclohexaminobenzothiazyl sulfide.

(2) *Dynamic moduli at 20° C (dynes × 10<sup>6</sup> per sq. cm.):*

Polymer Modulus	Natural rubber 20.6	Buna-S 31.1	Neoprene- GN 28.1	Neoprene- YD 34.8	Neoprene- Z 50.5	
Polymer Modulus	Hycar OR-15 43.3	Hycar OR-25 33.7	Thiokol- RD —	Per- bunan 32.9	Buna-N 35/65 36.6	Buna-N 25/75 32.0

(3) *Source of Polymers.*

The Buna-S, Perbunan and Buna-N were of American manufacture, the two latter polymers being distributed by Stanco Distributors Inc. The Hycar types are manufactured by the Hycar Chemical Co. (U. S. A.) and Thiokol-RD by the Thiokol Corp. (U. S. A.).

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# SOME LOW TEMPERATURE PROPERTIES OF ELASTOMERS\*

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## INTRODUCTION

Apparatus and techniques for the determination of Young's modulus of elastomers at low temperatures have been described in a previous publication<sup>1</sup>. The objects of the work described in the present report were: (1) to extend Young's modulus measurements to materials not previously studied, and (2) to present some preliminary data on creep phenomena at low temperatures. Improvements have been made in the apparatus since the original description was published and the test technique previously described has been simplified. A photograph of the present modified, assembled equipment is shown in Figure 1. A schematic sketch, showing details of the various mechanisms, is given in Figure 2.

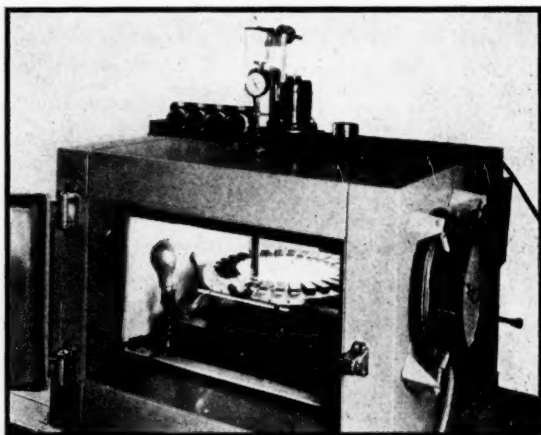


FIG. 1.—Photograph of apparatus.

It is well known that high-polymeric materials, such as Hevea rubber and most of the synthetic rubbers, under conditions of low strain, exhibit reversible, delayed elasticity. A result of this effect is that the application of a given, constant force (in bending a sample piece, for example) produces, not a fixed deflection, but rather one which depends on the duration of the force application. The total strain at any point in the sample, resulting from such force application, can be considered to be made up of two parts: one an instantaneous

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deflection independent of time and the other a creep strain dependent on time. It has been proposed<sup>2</sup> that such effects, together with associated stress relaxation effects, be referred to as primary creep phenomena.

The materials referred to above exhibit further creep effects under conditions of large strain, high temperatures, and extended times. Such effects result in plastic flow (under some conditions ultimately in failure), and are termed secondary creep phenomena. Inasmuch as separation of primary and secondary creep is extremely difficult at best, all observations reported in this work were made under such conditions that secondary creep was not present

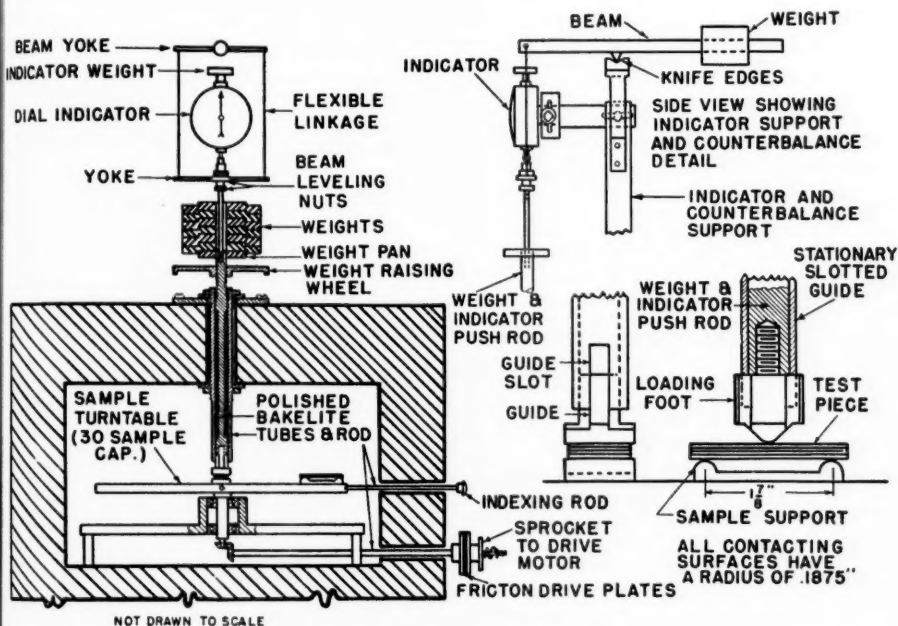


FIG. 2.—Schematic sketch of apparatus.

(or negligibly small). The data obtained can thus be interpreted in the light of primary creep theories alone.

### MODULUS MEASUREMENTS

To obtain useful and reproducible data on the bending modulus of Hevea and other elastomers, employing the apparatus shown, it was found expedient to allow a uniform time of ten seconds to elapse between the time of application of the dead load and the time the amount of the deflection was recorded. The Young's modulus calculated from these data consequently represents what might be termed a "ten-second Young's modulus" to distinguish it from the total and instantaneous moduli. The ten-second interval was arbitrarily chosen in the interests of both accuracy and convenience. Because of the rapid movement of the dial indicator needle immediately after application of the load, readings could not be obtained accurately until at least five to ten seconds had elapsed. In most instances motion of the dial indicator needle



after ten seconds was slow enough to ensure reasonable accuracy in reading. Longer loading periods would have been unnecessarily time-consuming.

In the apparatus, as originally designed, the loading mechanism (particularly the tubes and rods which extend through the walls of the cold chamber) was made of a phenol-formaldehyde resin. This material was selected to reduce transmission of heat and also to reduce the initial dead load on the sample. In spite of these precautions, the initial load totalled 368 grams. To keep the dead load deflection small at the higher temperatures, it was necessary to employ fairly thick test-pieces (approximately  $\frac{1}{2}$  inch), particularly in the case of soft, gum type of stocks. At low temperatures, however, excessively high loads were required to produce reasonable deflections on such

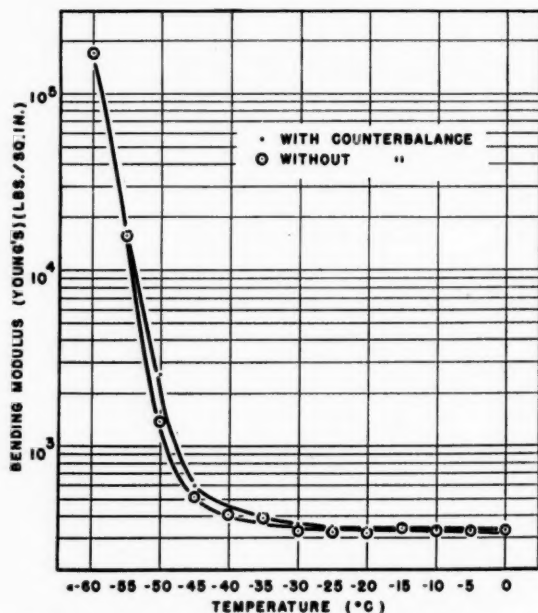


FIG. 3.—Effect of counterbalance on bending modulus values for Hevea stock A.

thick samples. To avoid this difficulty, two samples of each compound were placed in the unit during each run. Load-deflection observations were made on the thick samples at the higher temperatures and on the thin samples at the lower temperatures. Although this method gave quite satisfactory results, the capacity of the unit was thereby reduced. Furthermore, interpretation of low-temperature creep data would have been considerably complicated by the existence of this high initial load. The counterbalance, shown in Figure 2, was subsequently devised and adjusted to produce an initial load of 55 grams. It was not found feasible to reduce this initial load to zero, since experience indicated that a small amount of stress was necessary to overcome the slight tendency of some of the samples to warp or twist as the temperature of the test chamber varied. The effect of this change in initial load on the measured modulus is small, as can be seen from typical data shown in Figure 3. These data were obtained in the manner previously described<sup>1</sup>, except as noted on Figure 3.

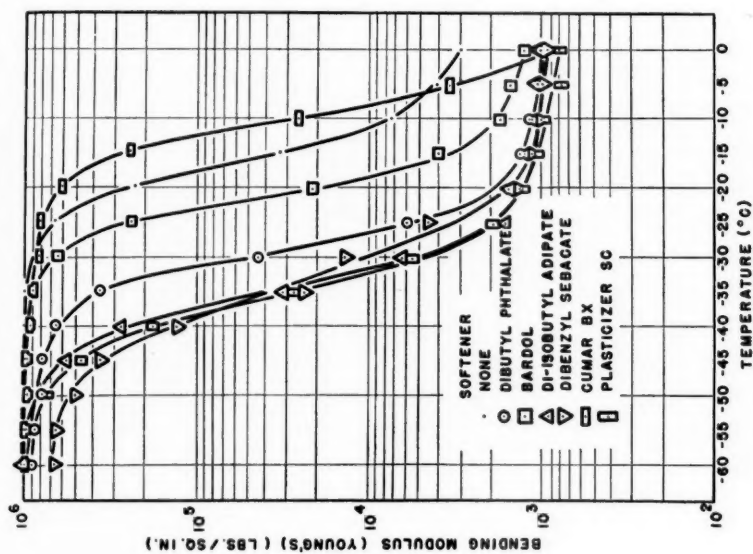


Fig. 5.—Young's modulus as a function of temperature; B/A type 2 stocks.

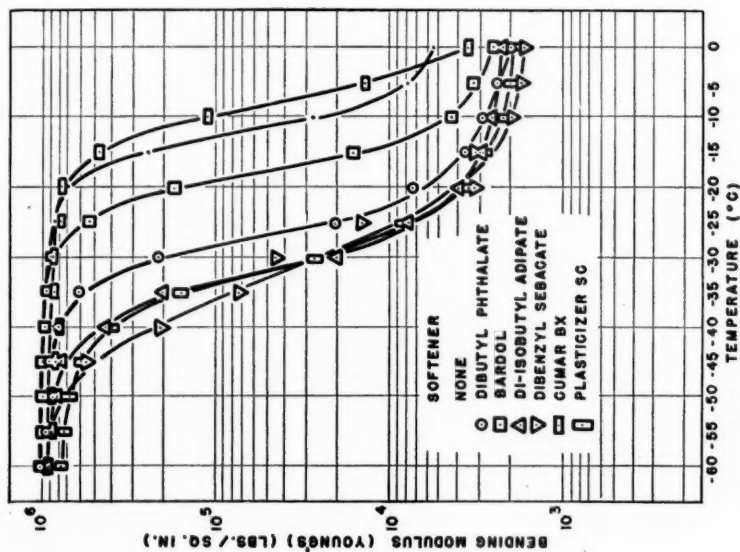


Fig. 4.—Young's modulus as a function of temperature; B/A type 1 stocks.

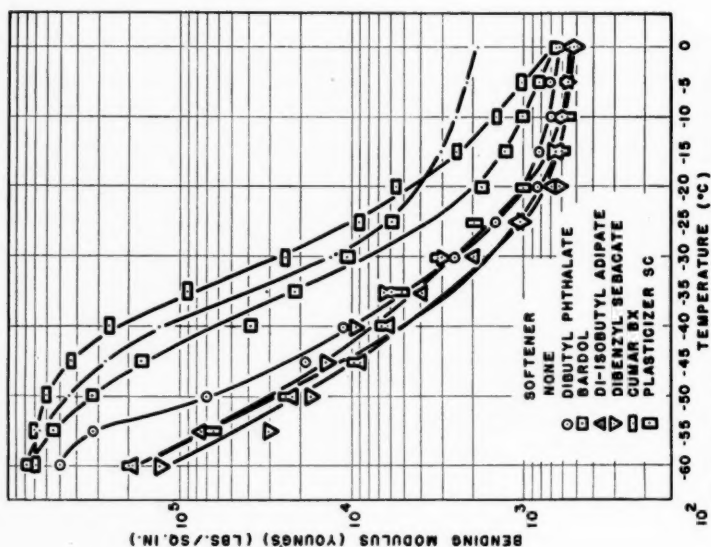


Fig. 7.—Young's modulus as a function of temperature;  
B/A type 4 stocks.

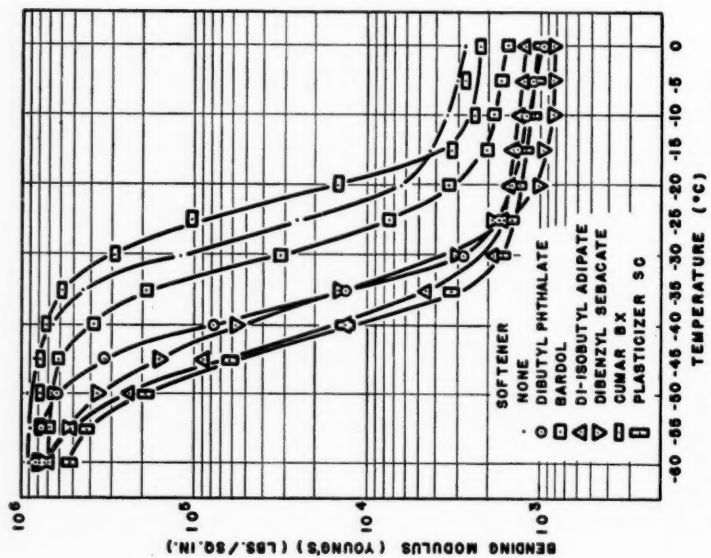


Fig. 6.—Young's modulus as a function of temperature;  
B/A type 3 stocks.

Corrections for indentation of sample and compression of loading rod were found to be a necessary part of the originally described technique because of the thick samples and relatively high loads employed. Introduction of the counterbalanced system eliminated the need for employing thick samples; hence the indentation corrections (formerly important at the higher temperatures) became small and negligible. Since the absolute values of the Young's moduli at extremely high values are of little commercial significance, the correction for compression of loading rod (important only at high values of moduli) was also considered unnecessary and was dropped when the counterbalance was installed. The data shown in Figures 4 to 9, inclusive, were obtained

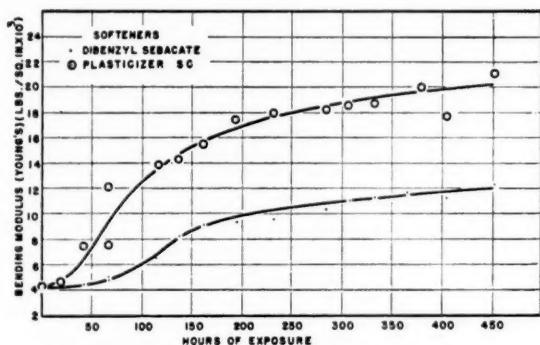


Fig. 8.—Time effect on B/A type 4 stocks at  $-35^{\circ}\text{C}$ .

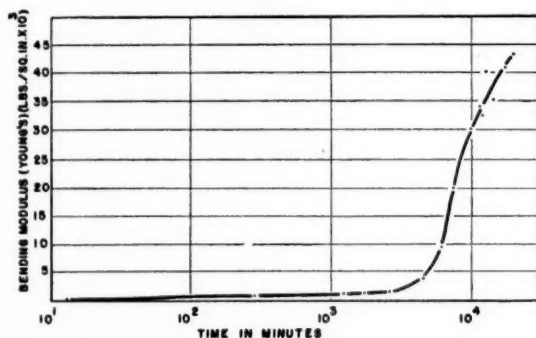


Fig. 9.—Time effect on uncured Hevea stock B at  $0^{\circ}\text{C}$ .

before the counterbalance was installed, and hence include all corrections described in the early technique. The data shown in the remaining figures were obtained on the counterbalanced apparatus, and are not corrected either for indentation of sample or compression of loading rod. A comparison of Figures 5 and 12 shows the effect of omitting these complicating corrections from data obtained with the counterbalanced system. It can be seen that the absolute values of Young's modulus obtained by the two techniques agree closely except at low temperatures, where the moduli are so high as to be of little or no practical value.

Unless specifically otherwise mentioned, all modulus data reported in this work were taken under conditions such that crystallization effects (resulting

from exposure to low temperatures) were negligibly small. The modulus changes observed are, hence, attributable to pure second-order transition phenomena, although it should be remembered that some of the materials might ultimately have shown further stiffening as a result of crystallization, if the tests had been continued over longer periods of time.

The low-temperature characteristics of stocks based on synthetic polymers depend not only on the chemical composition and physical nature of the polymer itself but also on the amount and nature of the pigments added. Data on the change in Young's modulus with change in temperature have previously been reported for a number of synthetic rubbers as well as Hevea<sup>1</sup>. It was shown that compounds having better low-temperature stiffening characteristics were obtained as the styrene content was progressively lowered in a butadiene-styrene type copolymer. A similar study has now been made with compounds based on the butadiene-acrylonitrile (*B/A*) type copolymer. Although not strictly alike in all respects (because of slight changes in the polymerization process), the major difference in the four elastomers tested is the variation in acrylonitrile content. The acrylonitrile content decreases in the order: *B/A* type 1, 2, 3, and 4. The effects of several typical softeners on the low-temperature stiffening characteristics of compounds based on these were also studied. The formulas of the stocks studied are shown in Table I. The Young's modu-

TABLE I  
GENERAL STOCK FORMULAS (FIGURES 4-7)

Polymer (as indicated)	100
Softener (as indicated)	20
Carbon black (SRF)	70
Zinc oxide	3
Sulfur	2.5
Benzothiazyl disulfide	1.0

lus (measured at the usual 10 seconds) *vs.* temperature curves obtained are shown in Figures 4-7.

Brittle-point temperatures, measured by a modification of the method of Selker, Winspear, and Kemp<sup>3</sup>, were determined on the same compounds. The results obtained are given in Table II.

TABLE II  
BRITTLE POINT TEMPERATURES (°C)—*B/A* TYPE COMPOUNDS

Copolymer type	1	2	3	4
<i>Softener</i>				
None	-17	-27	-41	-56
Dibutyl phthalate	-26	-34	-44	-55
Bardol	-22	-26	-38	-55
Diisobutyl adipate	-23	-34	-44	-56
Dibenzyl sebacate	-37	-43	-55	-63
Cumar-BX	-8	-16	-36	-47
Plasticizer-SC	-32	-40	-49	-60

By both modulus and brittleness types of test, it can be seen that improved low-temperature characteristics are progressively imparted to the *B/A* type copolymer as the amount of acrylonitrile present is reduced. Both tests also indicate that Cumar-BX, though effective as a softener at normal temperatures, stiffens rather than softens the compounds at low temperatures. Beyond this qualitative agreement there is little correlation between the results obtained by

TABLE III  
MODULUS (IN LBS. PER SQ. IN.) AT THE BRITTLE POINT  
TEMPERATURE OF EACH COMPOUND—B/A TYPE STOCKS

Copolymer type	1	2	3	4
<i>Softener</i>				
None	450,000	780,000	730,000	675,000
Dibutyl phthalate	36,000	260,000	275,000	325,000
Bardol	320,000	340,000	315,000	550,000
Diisobutyl adipate	5,300	27,000	50,000	85,000
Dibenzyl sebacate	125,000	260,000	550,000	200,000 (est.)
Cumar-BX	50,000	340,000	630,000	510,000
Plasticizer-SC	51,000	180,000	160,000	200,000

the two methods. For example, in Table III are listed the moduli of the several stocks tested, at the brittle-point temperature of each. These data indicate that some of the compounds become brittle (under the given conditions of impact velocity), even though their moduli, measured under nearly static conditions, remain reasonably low. On the other hand, the static moduli of some of the compounds are seen to be extremely high at their respective brittle-point temperatures. Inasmuch as the dynamic is nearly always higher than the static modulus, the moduli of the stocks tested (under almost any set of conditions to which rubberlike materials are subjected in service) would be even higher than those tabulated. The moduli of stocks employed as vibration dampers, motor supports, diaphragms, etc., range from 300 to approximately 3000 lbs. per sq. in. at normal temperatures. It is doubted that a compound having a static modulus much greater than 10,000 lbs. per sq. in. would be of much value as a rubberlike material in normal service. Hence this value is tentatively considered to be the maximum allowable modulus for rubberlike serviceability. The temperatures at which the several compounds tested attain a modulus of 10,000 lbs. per sq. in. are shown in Table IV. It will be

TABLE IV  
TEMPERATURE (° C) AT WHICH MODULUS IS 10,000 LBS. PER SQ. IN.—B/A TYPE STOCKS

Copolymer type	1	2	3	4
<i>Softener</i>				
None	- 7	-11	-22	-28
Dibutyl phthalate	-23	-26	-34	-40
Bardol	-14	-19	-26	-31
Diisobutyl adipate	-27	-31	-38	-44
Dibenzyl sebacate	-26	-30	-34	-42
Cumar-BX	- 4	- 8	-19	-25
Plasticizer-SC	-25	-32	-39	-45

observed that these temperatures are considerably higher than the corresponding brittle-point temperatures given in Table II. It is also interesting to note that, at the concentrations studied, only three of the softeners tested appreciably affected the brittle point temperatures of the B/A type 4 series, while all had a large effect on the brittle-point temperatures of the B/A type 1 series. When judged by modulus tests, however, the effectiveness of the softeners was nearly the same in all four series of compounds.

Of two compounds (both having brittle-point temperatures below the anticipated minimum temperature to which they might be subjected in service), the one having the lower modulus at the latter temperature would unquestionably be considered the better for low-temperature serviceability. The



advantages of compounds having extremely low brittle-point temperatures but very high moduli at temperatures even above the brittle point are not so clear. In applications, however, where the applied stresses are large enough to produce deflections in spite of the high modulus, the stock having the lower brittle point would probably be selected. In such an instance, the material would survive the initial deflection without failure, and would rapidly increase in temperature (and hence become more serviceable) as a result of subsequent deflections.

The data illustrate quite clearly the desirability of measuring both properties in evaluating the low-temperature serviceability of a compound.

Periodic checks are made during all test runs to make certain that crystallization stiffening is not contributing to the modulus changes being observed. A slight tendency toward progressive stiffening, with continued exposure to low temperatures, was noted during the run on the *B/A* type 4 series of compounds. A further study of this series was hence made.

The seven *B/A* type 4 stocks were placed in the cold chamber and held at  $-35^{\circ}\text{C}$  for a period of 452 hours. Two of the seven exhibited a marked progressive stiffening, while the others showed none whatever up to the conclusion of the test. The modulus changes observed are shown in Figure 8.

The observed increase in modulus is of a lower order of magnitude than that exhibited by Neoprene-GN (GR-M) or unvulcanized Hevea and may be the result of crystallization or hardening of the softener itself. It has also been suggested by R. H. Taylor<sup>4</sup> of the National Bureau of Standards that this particular stiffening effect may be the result of decreasing solubility of the softener in the polymer as the temperature is decreased. If this were the case, the modulus of a stock containing such a softener should, after long exposure, approach the modulus of a similar stock containing no softener. The tests have not been extended for periods of time long enough to prove this point. However, the fact that the modulus of the stock containing no softener had not been exceeded by either of the two stocks in question, up to the conclusion of the test, lends support to this hypothesis. Whether or not these two softeners have similar effects on the other *B/A* type copolymers has not been determined.

The effect of continued exposure to a temperature of  $0^{\circ}\text{C}$  on the bending modulus of a compound having a Hevea rubber base is shown in Figure 9. The formula of this compound is given in Table V. Only the unvulcanized sample of Hevea exhibited this effect up to the conclusion of this test. Samples cured 40 to 80 minutes at  $270^{\circ}\text{F}$  (the latter corresponding to a technical optimum cure) showed no observable progressive stiffening in this test. A comparison of Figures 8 and 9 illustrates the difference (mentioned earlier) in the magnitudes of the effect attributable to crystallization of the elastomer itself and that resulting from the use of a particular softener in a base elastomer which, in the absence of the softener, shows no crystallization stiffening.

Thiokol-FA, like Neoprene-GN and unvulcanized Hevea rubber, exhibits pronounced time-stiffening effects. Consequently, special precautions had to be observed in obtaining Young's modulus *vs.* temperature data to make certain that the modulus changes observed were caused entirely by second-order transition effects. The results of tests conducted under such conditions are shown in Figure 10 for typical "gum" and SRF (semireinforcing furnace) black type of stocks. The formulas of the stocks tested, together with brittle-point temperatures, are shown in Table V. No attempt was made to evaluate the crystallization stiffening effect in the case of these two stocks, though indications were that it would be quite pronounced.

The effect of temperatures on the ten-second Young's modulus of polybutadiene compounds has been reported previously<sup>1</sup>. Although not specifically denoted as such at the time, the polymer employed then was made by an emulsion polymerization process. Since these results were published, a similar study was made of compounds based on mass (sodium) polymerized polybutadiene. The formulas of the compounds tested are the same as those previously employed and are given in Table V. Brittle-point temperatures are also given in Table V. The modulus *vs.* temperature data obtained, given in Figure 11, show that the two methods of polymerization produce polymers hav-

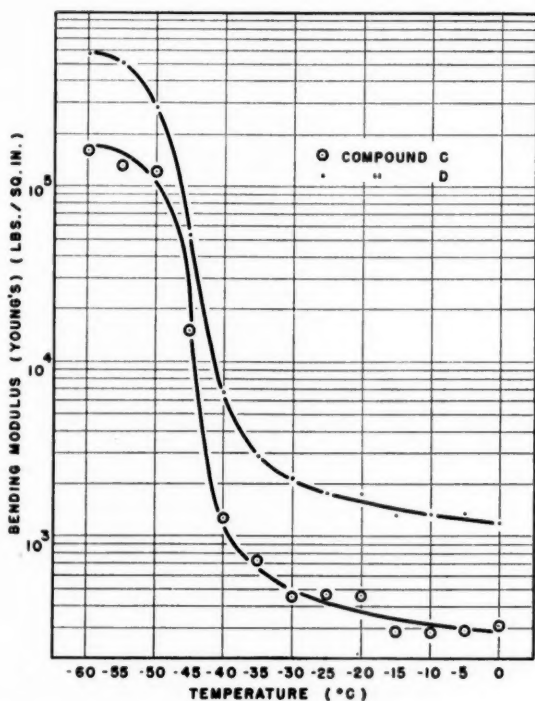


Fig. 10.—Young's modulus as a function of temperature—Thiokol-FA stocks.

ing radically different low temperature stiffening characteristics. Chemical analyses indicate<sup>5</sup> that the molecular structure of a polymer is affected by a change in the method of polymerization or a variation in the amount of controlling agent present. It is reasonable to expect that the modulus of an elastomer would depend on the molecular structure of the material. Hence, though the data are not sufficient to be conclusive, it is suggested that studies of this type might be useful in following changes in molecular structure as a function of the various steps involved in the polymerization process.

#### PRIMARY CREEP AT LOW TEMPERATURES

The primary creep behavior of plastic materials has been the subject of many extensive researches, an excellent survey of which is given in Leaderman's

TABLE V  
STOCK FORMULAS AND BRITTLE-POINT TEMPERATURES. THIOKOL-FA, MASS AND EMULSION POLYMERIZED POLYBUTADIENE,  
HEVEA-RUBBER COMPOUNDS

Stock designation	A	B	C	D	E	F	G	H
Hevea rubber	100	100						
Thiokol-FA			100	100	100	100	100	100
Emulsion-polymerized butadiene								
Mass-polymerized butadiene								
Sulfur	3	3			2	2	2	2
Zinc oxide	3	3	10	10	5	5	5	5
Stearic acid	0.5	3.5	0.5	0.5	0.5	3	0.5	3
Mercaptobenzothiazole	1.0	1.0			1.5	1.5	1.5	1.5
Benzothiazyl disulfide			0.3	0.3				
Diphenylguanidine			0.1	0.1				
Pine tar		3.0						
Bardol						5		5
Phenyl- $\beta$ -naphthylamine	1.0	1.0						
SRF black				40				
HPC black		50				50		50
Optimum cure	75' @ 270° F	75' @ 270° F	40' @ 298° F	40' @ 298° F	100' @ 270° F	100' @ 270° F	100' @ 270° F	100' @ 270° F
Brittle-point temperature (°C)	-53	-53	-43	-37	< -74	< -74	-40	-41

treatise<sup>2</sup>. In recent years similar studies, both theoretical and experimental, have been made on rubberlike materials by Hulburt, Harman, Tobolsky, and Eyring<sup>6</sup>, Simha<sup>7</sup>, Anthony, Caston, and Guth<sup>8</sup>, Eley<sup>9</sup>, Tobolsky and Eyring<sup>10</sup>, Tuckett<sup>11</sup>, and Kobeko, Kuvshinsky, and Gurevitch<sup>12</sup>. Most of the theoretical work has been centered on the constant strain (stress relaxation) type of experiment since, as Leaderman points out, this type of test is most amenable to theoretical interpretation. The creep data reported in the present work were obtained under constant applied load rather than constant strain conditions, and attempts are now being made to formulate theories based on this type of test. One of the results of this study has been the establishment of a creep

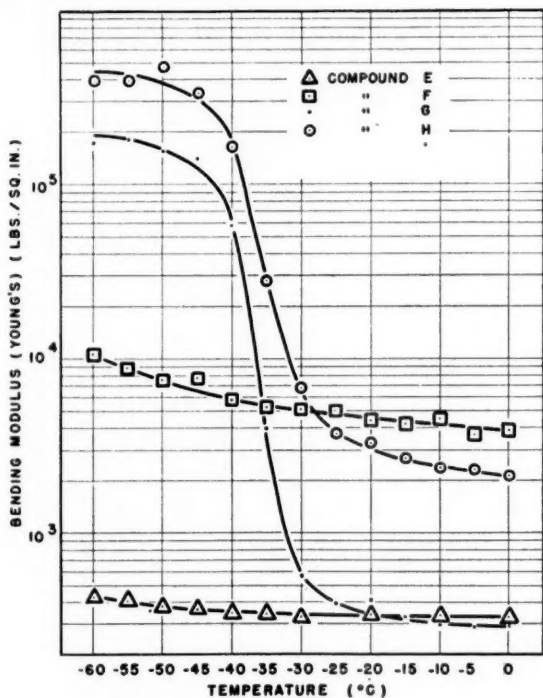


FIG. 11.—Young's modulus as a function of temperature—emulsion- and mass-polymerized polybutadiene.

constant, based on experimentally determined quantities, which can be employed as a convenient index of low temperature serviceability of a compound.

At temperatures around 30° C, the ten-second modulus discussed above approaches the so-called total modulus. At low temperatures, *i.e.*, under conditions such that primary creep takes place very slowly, the ten-second modulus is nearly identical with the instantaneous or (according to Kobeko) the acoustic modulus. At intermediate temperatures, the measured ten-second modulus depends, in varying degree, on both total and instantaneous moduli. According to the rather meager experimental data available, both total and instantaneous moduli are very nearly independent of temperature.<sup>5</sup> The results of some tests on a *B/A* type 3 stock (containing no softener),

shown in Figure 12, confirm these conclusions. In this test, the Young's moduli at several loading times were measured as a function of temperature. At 0° C, most of the ultimate deflection, including primary creep, had taken place even before the ten-second measurement was taken. Consequently there is little difference between the ten-second and six-minute moduli, *i.e.*, both approach the total modulus which in turn appears to be approaching a steady value at a temperature close to 0° C. At -60° C, only the instantaneous deflection and very little primary creep had taken place even after six minutes' loading. Hence very little difference in the moduli measured at the various loading times is again indicated. At intermediate temperatures the deflection measured at the ten-second loading time, for instance, includes only a part of the primary creep. Part of this creep takes place in the interval ten seconds to six minutes. Consequently, the two moduli are found to be considerably different.

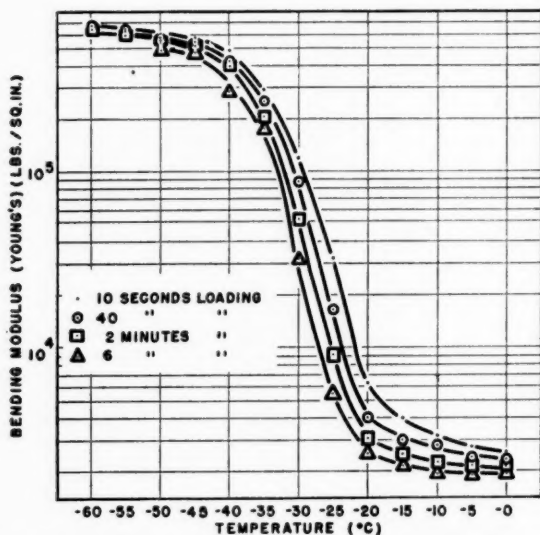


Fig. 12.—Effect of loading time on Young's modulus of B/A type 3 stock containing no softener.

It is this intermediate temperature, at which the ten-second modulus begins to depend on, or approach, the instantaneous modulus (as the temperature of the sample is lowered) which can be employed as a serviceability index. At temperatures well above this point, the measured ten-second deflection includes the deflection corresponding to the instantaneous modulus, plus a considerable amount of the deflection resulting from primary creep. In other words, the material at these temperatures responds relatively quickly to impressed forces and consequently possesses usable, rubberlike properties. At temperatures below this point, primary creep takes place very slowly, the measured ten-second modulus is high, and hence the material exhibits the characteristics of stiff plastic materials rather than those of rubberlike materials.

Following Leaderman's notation, the total deflection of a simple beam after being loaded for a time  $n$  can be written:

$$D_n = \frac{FL}{E} \{1 + C\psi(n)\} \quad (1)$$

where  $F$  is a form factor,  $L$  is the total applied load,  $E$  is the instantaneous modulus,  $C$  is a constant, and  $\psi(n)$  is the creep factor (a function of time).

Now for a simple beam of rectangular cross-section:

$$E = \frac{Ll^3}{4wt^3(\Delta R)} \quad (2)$$

where  $E$  is the instantaneous modulus,  $L$  is the total applied load as in (1) above,  $l$  is the distance between beam supports,  $w$  is the width of sample,  $t$  is the thickness of sample, and  $(\Delta R)$  is the instantaneous deflection.

The form factor  $F$ , in this case, from (2) is given by:

$$F = \frac{l^3}{4wt^3} \quad (3)$$

hence:

$$D_n = \Delta R \{1 + C\psi(n)\} \quad (4)$$

For any given time of loading,  $C\psi(n)$  will be a constant which can be denoted by  $C_n$ . Hence from Equation (4) above we obtain:

$$C_n = \frac{D_n - (\Delta R)}{(\Delta R)} \quad (5)$$

The term  $(\Delta R)$  in Equation (5) represents the instantaneous deflection which cannot be accurately determined experimentally except at very low temperatures. If the ten-second deflection be substituted in an equation of the form of (5) above, we can define a modified, or experimental, creep constant by the expression:

$$C_n' = \frac{D_n - \Delta R_{10}}{\Delta R_{10}} \quad (6)$$

At relatively high temperatures the values of  $C_n'$  are low, since  $D_n$  is only slightly greater than  $\Delta R_{10}$ . Similarly at very low temperatures, even though  $\Delta R_{10}$  is small compared with its value at higher temperatures,  $C_n'$  is relatively small since  $D_n$  is only slightly greater than  $\Delta R_{10}$ . At some intermediate temperature, where  $D_n$  is significantly greater than  $\Delta R_{10}$ , i.e., a large part of the primary creep takes place in the time interval ten to  $n$  seconds, the value of  $C_n'$  will reach a maximum. In the region of the temperature at which this maximum in the experimental creep constant occurs, the ten-second deflection under a given applied stress decreases rapidly with decrease in temperature. In addition, primary creep rate is reduced sharply, so the character of the material changes from a soft, rubberlike substance which is easily and quickly deformed by stress application to a hard, (and sometimes brittle) substance which is deformed with difficulty.

By definition:

$$D_n = R_n - R_0 \quad (7)$$

and

$$(\Delta R_{10}) = R_{10} - R_0 \quad (8)$$

where  $R_n$  and  $R_{10}$  are the dial-gauge readings at a time  $n$  and 10 seconds respectively, and  $R_0$  is the zero load dial-gauge reading obtained in the manner previously described. Hence from Equations (6), (7), and (8), we may write:

$$C_n' = \frac{R_n - R_{10}}{R_{10} - R_0} \quad (9)$$



The expression above presumes the load corresponding to  $R_0$  to be zero. In fact, even with the counterbalanced system, the initial load is 55 grams. At the higher temperatures, the load added to obtain  $R_{10}$  may in some instances be of the same magnitude as the initial load. The difference between  $R_{10}$  and  $R_0$  as experimentally determined on the present apparatus is hence smaller than it should be by the ratio of the loads employed in the two cases (assuming Hooke's law to hold as a first approximation). The denominator in Equation (9) above should hence be written:

$$(R_{10} - R_0) \times \frac{L + 55}{L} \quad (10)$$

The numerator requires no such correction, since both  $R_n$  and  $R_{10}$  are measured with the total load applied. The experimental creep constants measured and plotted as a function of temperature were thus calculated from the final expression:

$$C_n' = \frac{R_n - R_{10}}{R_{10} - R_0} \times \frac{L}{L + 55} \quad (11)$$

Experimental creep constants have been determined for the same series of B/A type stocks described earlier. The results are shown in Figure 13 for

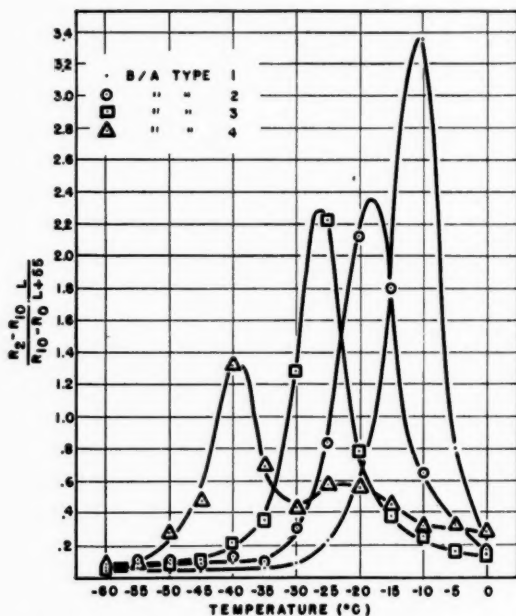


Fig. 13.—Creep constants of B/A type stocks, containing no softener, as a function of temperature.

the stocks containing no softeners. The temperatures at which the maximum creep constant occurs are given in Table VI together with the temperatures at which the moduli of the same stocks reached a value of  $10^4$  lbs. per sq. inch. It can be seen that a reasonably constant difference in temperature exists be-

TABLE VI

CRITICAL TEMPERATURES ( $^{\circ}\text{C}$ ) FOR *B/A* TYPE STOCKS CONTAINING NO SOFTENERS

Copolymer type	1	2	3	4
@ Modulus $10^4$ lbs. per sq. in.	-6	-11	-22	-28
@ Maximum creep constant	-11	-18	-26	-39

tween the two indices, except for the *B/A* type 4 stock, which exhibits a small, secondary maximum at a relatively high temperature.

The data shown in Figure 13 were calculated from ten- and 120-second deflection readings. Creep constants were also calculated for one of the stocks (*B/A* type 3, no softener) for several different time intervals. These data, shown in Figure 14, illustrate the reproducibility and accuracy obtainable by this experimental method and analysis.

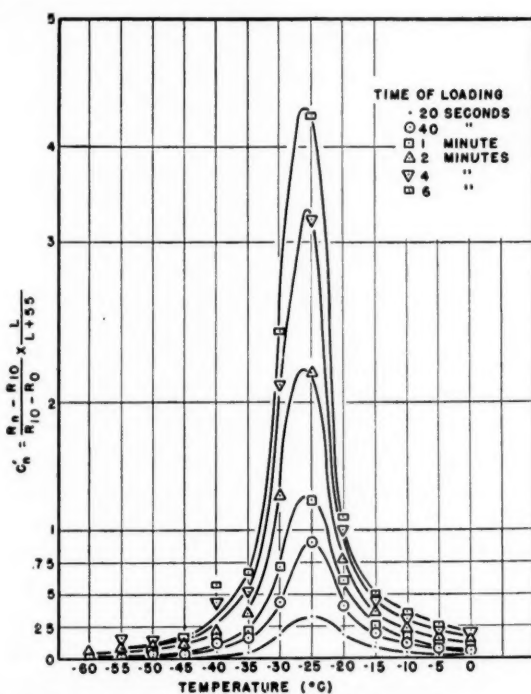


Fig. 14.—Creep constants for *B/A* type 3 stock containing no softener, at various loading times, as a function of temperature.

The effect of some softeners on the creep constants of one of the stocks is shown in Figure 15. The temperatures at maximum creep constant and at a modulus of  $10^4$  lbs. per sq. in. are given in Table VII. As in the instance above,

TABLE VII

CRITICAL TEMPERATURES ( $^{\circ}\text{C}$ ) FOR *B/A* TYPE 3 STOCKS CONTAINING VARIOUS SOFTENERS

	No softener	Dibutyl phthalate	Bardol	Diisobutyl adipate	Di-benzyl sebacate	Cumar-BX	Plasticizer-SC
@ Modulus $10^4$ lbs. per sq. in.	-22	-34	-26	-38	-34	-19	-39
@ Maximum creep constant	-26	-38	-30	-41	-36	-21	-42

the differences in the two sets of temperatures are quite constant, the maximum creep constant temperatures again being somewhat lower than those derived from the  $10^4$  lbs. per sq. in. modulus values.

Creep factors having greater theoretical importance than the creep constants discussed earlier can also be calculated from the data obtained if Kobeko's hypothesis (that the instantaneous modulus is independent of tempera-

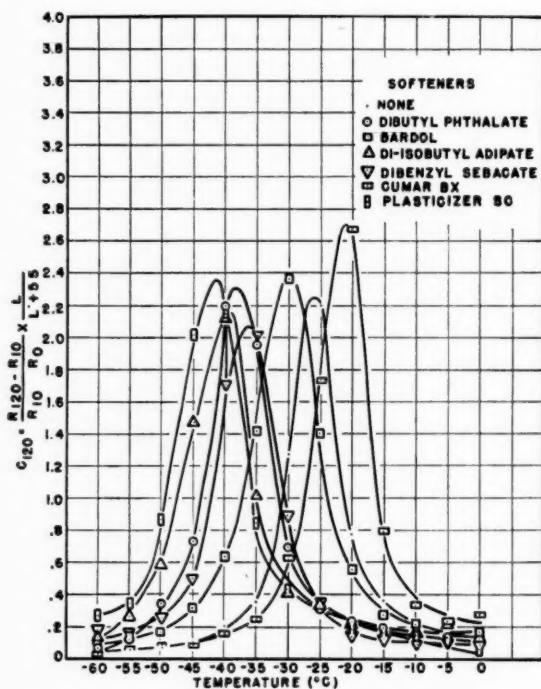


Fig. 15.—Creep constants for B/A type 3 stocks as a function of temperature.

ture) is accepted. If, in Equation (1) above, we write:

$$C\psi(n) = C_n \quad (12)$$

for any given time of loading, we obtain:

$$C_n = \frac{D_n E}{FL} - 1 \quad (13)$$

If we assign to  $E$  in the above expression the value calculated from deflection observations made at extremely low temperatures, then creep factors can be calculated from the observed total deflections  $D_n$ . Typical data obtained in two B/A type 3 stocks and calculated by this method are shown in Figure 16, for a 120-second loading period. Although a definite difference between the two stocks tested is shown by this method of analysis, the possibility of employing these results in some way as a practical serviceability index is not

readily apparent. Since, however, this analysis is based on more rigorous theoretical grounds than the experimental creep constant methods<sup>13</sup>, these data should be of more interest to the theoretical analyst.

### SUMMARY OF RESULTS

The low-temperature Young's modulus of copolymers of the butadiene-acrylonitrile (B/A) type was found to be lowered by a reduction in the acrylonitrile content of the copolymer.

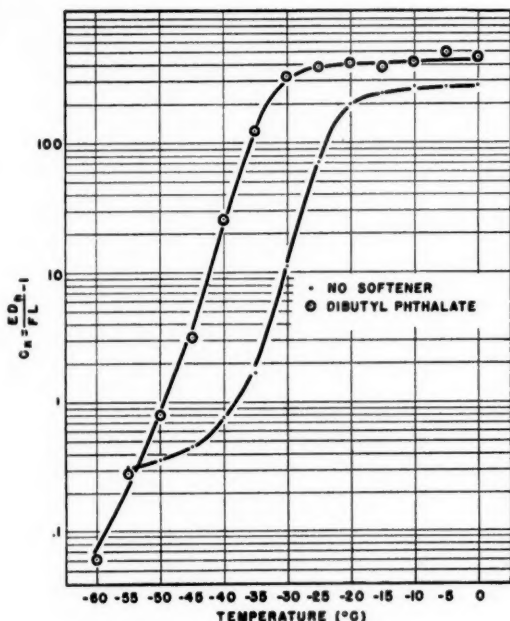


FIG. 16.—Creep factors based on two-minute loading time using  $-60^{\circ}\text{C}$  modulus value for  $E$ .

Mass- and emulsion-polymerized butadiene were found to possess considerably different low temperature physical characteristics.

Certain plasticizers (employed to improve low-temperature properties) imparted a time-stiffening effect to compounds which, in the absence of the given plasticizer, showed no time effect.

An experimental method for the measurement of primary creep of elastomers at low temperatures is described. Calculation of a creep constant, as defined, appears to yield a critical temperature which may be useful as a serviceability index.

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# ELECTROSTATIC PROPERTIES OF RUBBER AND GR-S\*

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Careful observations on the triboelectrification of rubber by a number of investigators<sup>1</sup> have disclosed many discrepancies and anomalies. A large number of these can be traced back to inadequate measuring devices and to the fact that the surface charge or contact potential on rubber does not spread uniformly over the surface, but is usually spotty because of surface irregularities and incomplete contact with the other contacting member.

As is well known, when two dissimilar materials are rubbed or pressed together and then separated, equal and opposite charges are produced on the two materials. The amount of charge, as well as the sign, depend on the nature of the contacting surfaces<sup>2</sup>. By pressing various materials together, separating, and then measuring the magnitude and sign of the charge, a triboelectric or contact potential series<sup>3</sup> can be arranged. Rubber is at the negative end of the list, while certain complex resinous organic materials are at the most positive end of the series. Since like charges are known to repel while unlike charges are known to attract, we might expect that if a highly positive material is milled into rubber, which is itself very negative, that a very strong electrostatic bond would result and might give rise to reinforcement of the rubber. In fact, the tensile strength of pure-gum GR-S stocks which have a normal tensile strength of 14 kg. per sq. cm. has been increased to 77 kg. per sq. cm., while the tensile strengths of high zinc compounds have been increased from 70 to 121 kg. per sq. cm. by the addition of highly positive organic compounds.

It is the purpose of this paper to describe a new electrostatic modulator which is used in conjunction with a standard audio amplifier and output meter to measure the contact potentials of rubber and GR-S, both compounded and uncompounded, and also certain compounding ingredients; and to point out further that there is apparently a partial correlation between the electrostatic behavior of these materials and the reinforcement of both rubber and GR-S.

## VACUUM-TUBE VOLTMETER

To overcome the disadvantages of the gold leaf electroscope, which are well known, attempts have been made to utilize the high gain of vacuum tubes. These devices are fine for indicating the sign of the charge, but they are of little value for measuring the magnitude of an electrostatic charge. For example, when a sample of crude rubber, having a clean, smooth, and uncharged surface, is brought into intimate contact with a similar sample of GR-S, electronic rearrangement takes place, and when the samples are separated, the GR-S has a negative charge and the rubber has a positive charge. In other words, the GR-S robs the rubber of a certain number of electrons, making it negative, and the loss of these electrons in turn leaves the rubber positive.

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The sign of the charge can be determined by holding the contacted and charged surfaces of the samples up to a 7.5-cm. diameter metal plate attached to the free grid of a V.T.V.M. such as the one shown in Figures 1 and 2. When

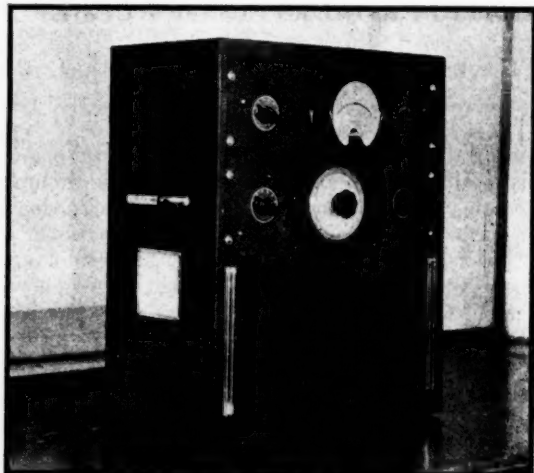


Fig. 1.—Vacuum-tube voltmeter.

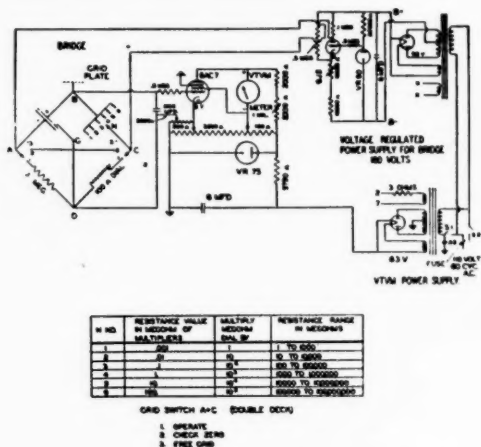


Fig. 2.—Schematic wiring diagram of vacuum-tube voltmeter and megohm bridge.

the rubber sample is brought up to the grid plate, the meter needle moves to the right, indicating a positive charge. When the GR-S sample is brought up to the grid plate, the meter needle moves to the left, indicating a negative charge.

The samples can be deionized (decharged) before contact with each other by exposing them to an open flame. When completely deionized, they should produce no deflection of the V.T.V.M. when brought up close to the grid plate.

These same experiments can be repeated with disks (4 cm. diameter) of

cured stocks died out from tensile sheets cured in chromium-plated molds. In this case also, the rubber is positive to the GR-S.

While the sign of the charge can be determined with this instrument, the magnitude cannot be measured, as the needle soon returns to zero because of leakage in the grid circuit, even though the charged rubber sample has not been moved relative to the grid plate, and is still charged.

#### VIBRATING GRID TYPE INSTRUMENTS

Early in our electrostatic work we discovered that when the meter reading started to drop it could be maintained either by moving the charged sample closer to the grid plate or by moving the grid plate closer to the sample. This led to experiments with a device in which the sample was mounted on the face plate of a lathe and a small high speed grinder positioned on the power-driven cross feed so that the sample could be buffed accurately. The grid plate, which was connected to the grid of an audio amplifier, was mounted on the lathe bed about 0.5 cm. from the rubber test-specimen so as to pick up the charge developed by buffing or the contact potential between buffing wheel and sample. This apparatus was only fairly satisfactory. A photograph of this apparatus is shown in Figure 3. The grid plate pick-up is not shown, as this set-up is

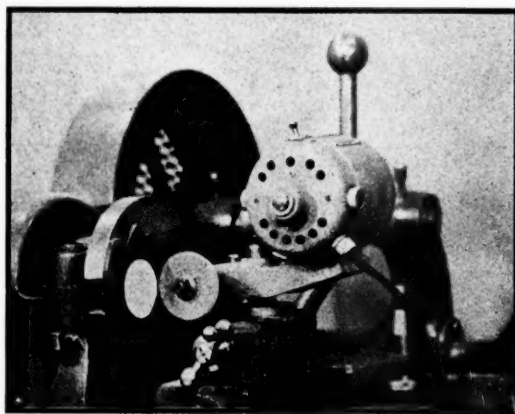


Fig. 3.—Lathe buffing set-up.

used only for precision buffing of the samples before regular contact potential tests.

To obtain a steady meter reading and also do away with the necessity of a high-gain direct-coupled d.c. amplifier, the vibrating grid type electrostatic voltmeter<sup>4</sup> has been developed which utilizes a high-gain a.c. amplifier. In this device the capacity between the charged sample and the vibrating grid plate, which is connected to the grid of the a.c. amplifier, is continually changing at audiofrequency so that the original electrostatic potential or charge on the specimen is changed in effect into an alternating voltage which is easily amplified by the high-gain a.c. amplifier. In this apparatus it is difficult to control the amplitude of the vibration to narrow limits, and any change caused by damping of the apparatus and resonance greatly affects the accuracy of measurement. Adequate shielding of the vibrator and grid circuits is also difficult.

## ELECTROSTATIC MODULATOR

In our new electrostatic modulator, the electrostatic lines of force between the charged specimen and the stationary grid plate are cut at audiofrequency (300 cycles per second) by a small motor-driven four-bladed fan. This produces in effect an alternating current voltage of approximately sine wave to the audio amplifier. The output can be connected to a speaker and heard as a hum, observed on the cathode-ray oscillograph, or, preferably, it can be observed on a regular output meter, so that accurate quantitative data can be obtained. The greater the charge on the sample, the stronger the resulting electrostatic field and the greater the amplitude of the resulting voltage furnished to the a.c. amplifier. Extremely minute charges can be measured with this device, such as the charge put on a sample of rubber by merely touching it, and the charge on a Lucite rod can be detected at a distance of 10 or 15 feet. The range and sensitivity of the instrument can be varied by the distance of sample from grid plate and by the gain controls on the amplifier. Since the grid plate is stationary, the apparatus does not suffer from resonance and shielding difficulties.

A photograph and line drawing of the electrostatic modulator are shown in Figures 4 and 5.

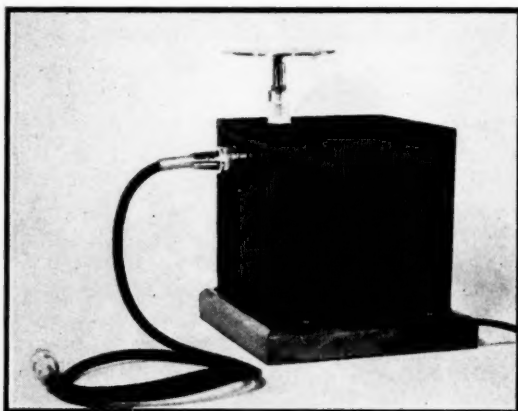


Fig. 4.—Electrostatic modulator.

This unit can be plugged into the microphone input of an ordinary public address system, and electrostatic charges can be heard as a hum in the loud-speaker when the charged sample is brought near the charge plate, or the charge plate can be replaced by a cup and the charged sample dropped into the cup.

## CONTACT POTENTIAL APPARATUS

Our apparatus for measuring the contact potential of rubber sheets is shown in the photograph—Figure 6—and the line drawing—Figure 7.

It will be noted that it consists of four main parts.

I. The metal specimen holder which is mounted on a Lucite or polystyrene insulator.

II. The mirror surfaced steel plunger which contacts the sample and acts as the reference surface against which the contact potential is measured.

Lucite or polystyrene insulation is used to insulate completely the plunger. Means are provided to press the plunger down against the rubber test-specimen with a constant force provided by the primary and secondary springs. Quick release of the plunger from the test-specimen is obtained by the use of the stiff springs and the latch at the top of the sliding plunger shaft. The average velocity of the plunger is 225 cm. per second. The spring exerts a pressure

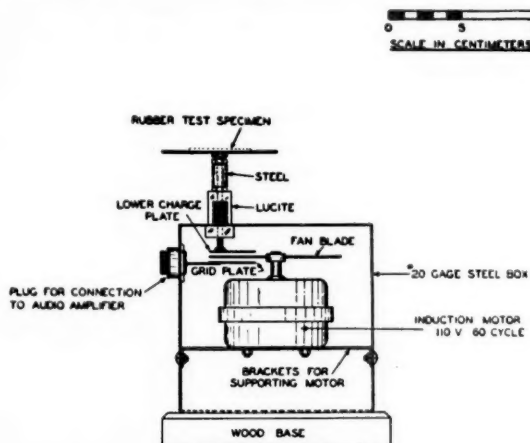


FIG. 5.—Electrostatic modulator.

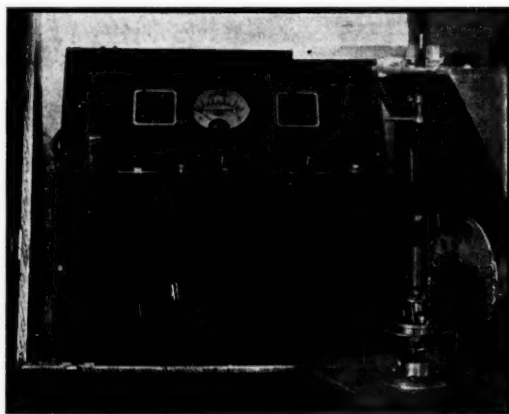


FIG. 6.—Electrostatic contact potential apparatus.

of 1.58 kg. per sq. cm. on the test-specimen which is a disk 4.13 cm. in diameter and 0.19 cm. thick. The specimen is held in place by the ring and thumb nuts. Occasional arcing was detected between the charged sample and the holder ring, and also in some cases the test-specimen partially stuck to the plunger and was pulled slightly away from the sample holder. When this occurred a plus charge was of course, put on the sample holder, and this neutralized the negative charge already on it and gave an abnormally low contact potential reading. To eliminate this trouble, a smaller disk, 2.54-cm. in diameter, was used, and it

was cemented into the holder with Vulcalock cement. The presence of the cement did not alter the contact potentials. The plunger pressure on the smaller sample was 2.5 kg. per sq. cm.

Quick release of the plunger is very important, as the quicker the release the higher the contact resistance and the less chance of electrical leakage, which would lower the contact potentials.

III. The electrostatic modulator is built into this apparatus. The charged sample charges the sample holder, and electrostatic lines of force are set up between the charge plate and the grid plate. The fan cuts these lines of force or modulates them at audiofrequency, which in effect produces an a.c. wave which is amplified by the audio amplifier.

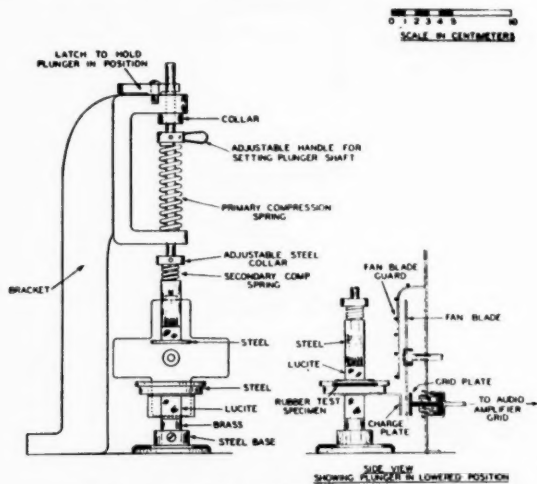


Fig. 7.—Electrostatic contact potential apparatus.

IV. The audio amplifier schematic is shown in Figure 8. While any good audio amplifier such as one used in commercial public address systems is suitable, the amplifier used was made in our own laboratory and designed especially for this use. The grid bias for the 6J7 input stage is supplied by a one-volt bias cell, and the input resistance, which is ordinarily around 5 megohms has been removed to give a better impedance match to the modulator unit. The input stage must be completely shielded. The 6N7, which is a dual-triode tube, is used as a phase inverter and second audio. The grid circuit of this second audio is provided with a selector switch so that various values of grid resistance can be switched in so as to take care of a wide range of input voltages and still obtain nearly full scale deflection on the output meter for all ranges.

The output stage consists of two 6L6 beam power tubes which operate in push-pull.

Instead of using the customary copper oxide rectifier in the output meter, a tube rectifier was used.

The amplifier was made to have a linear response so that the output meter readings would be directly proportional to the input voltages and electrostatic charges on the test-specimens. Calibration was obtained by the use of an audio oscillator and vacuum-tube voltmeter.

This amplifier has a gain of 110 db and a power output of 20 watts.

## EXPERIMENTAL PROCEDURE

## SAMPLE PREPARATION

Before contact potentials can be obtained on rubber samples, the specimens must have a clean, smooth, uncharged surface. This is very difficult to obtain, as, if anything is used to clean the surface such as a clean cloth and solvent, a contact potential will be set up between the cloth and specimen and also between the solvent and specimen. The solvent also may make the surface of the specimen more mobile so that electrostatic rearrangement may take place more easily, resulting in greater contact potentials. The cloth may leave particles of lint on the surface which will charge up and which may also serve

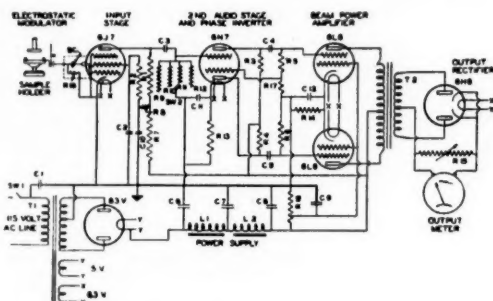


FIG. 8.—Schematic wiring diagram of the audio amplifier.

## Circuit constants of audio amplifier.

$C_{1,2,3,4,5} = 0.1 \mu\text{f}$ 600 v d.c.	$R_9 = 100 \text{ ohms}$	1W.	$T_1 = \text{Power transformer input}$
$C_{6,7,8,9,10} = 8 \mu\text{f}$ 600 v d.c.	$R_{10} = 500 \text{ ohms}$	1W.	115 v a.c. Output—350-0-
$C_{11,12} = 50 \mu\text{f}$ 50 v d.c.	$R_{11} = 1000 \text{ ohms}$	1W.	350, 5, 6.3 v a.c.
$L_{1,2} = 30 \text{ henry}$ 150-ma choke coil.	$R_{12} = 500 \text{ M ohms}$	1W.	$T_2 = \text{Output transformer } 6L6^2$
$R_1 = 200 \text{ M ohms}$	$R_{13} = 3000 \text{ ohms}$	5W.	p.p. to 30 ohms.
$R_2 = 1 \text{ megohm}$	$R_{14} = 200 \text{ ohms}$	20W.	$SW_1 = \text{power switch for } 110 \text{ v}$
$R_{3,4} = 100 \text{ M ohms}$	$R_{15} = 60 \text{ ohms}$	10W.	a.c.
$R_{5,6} = 500 \text{ M ohms}$	$R_{16} = 25 \text{ M ohms}$	50W.	$SW_2 = 4\text{-tap switch, rotary,}$
$R_{7,8} = 25 \text{ M ohms}$	$R_{17} = 15 \text{ M ohms}$	1W.	well insulated.
	$R_{18} = 5 \text{ megohms}$	0.5W.	Output meter = 0-1 milliam-
			pere.
			B. C. = 1 volt bias cell.

as focal points for point discharges of the charge on the specimen itself. When the sample is picked up from the table or, in fact, if it is in contact with any material, electrostatic charges are set up when the sample is moved. This makes it extremely difficult to obtain suitable specimens for testing. In addition to dust, lint, and other foreign matter which may contaminate the surface certain compounding ingredients such as sulfur, accelerators, stearic acid, etc., may bloom to the surface and alter completely the contact potential. There is also the possibility of skin effects and pigment segregation which may cause trouble. One method of overcoming these difficulties is to use buffed samples as suggested by Liska<sup>5</sup>. Our lathe set-up for precision buffing is shown in Figure 3.

While fairly good data have been obtained with buffed specimens, especially with carbon black stocks where it is usually essential, buffing has one serious disadvantage. It produces a rough surface of unknown and variable surface area for testing.

Fairly good results have been obtained by curing the samples in clean chromium-plated molds. However, care must be taken to avoid touching the samples, and they must be kept between Holland (linen) sheets in a desicca-



tor. In addition, the samples must be tested shortly after cure before blooming has a chance to occur.

In some cases it is, of course, necessary to clean the surface with freshly distilled acetone or ether with a clean, lint-free cloth. If a slight excess of acetone is used, the sample usually remains uncharged. Benzene or alcohol should not be used as the samples may be difficult to charge because of difficulty in removing the last traces of residual solvent, which may contain moisture. It is necessary in some cases to discharge the sample with a free flame. Acetone should not be used on uncured rubber or Buna-S specimens as it softens the polymer so that a clean separation between plunger and polymer cannot be made. This sticking of part of the sample to the plunger gives low contact potential results.

#### TESTING PROCEDURE

A 2.54-cm. diameter disk is died out from a tensile sheet 0.19 cm. thick, and the specially prepared or buffed sample is cemented in the sample holder with Vulcalock cement. The plunger and sample holder are discharged by momentarily touching with a grounded wire. The plunger is brought into contact with the test-specimen by pushing down on the plunger handle until the latch can be swung over the top end of the plunger shaft holding it in place. The metal plunger is now touched with the ground wire, and if the sample is not properly prepared and has an initial charge, before placing it in the holder, a reading will be observed on the output meter. The specimen holder is then discharged by momentarily touching it with the ground wire. This, of course, brings the meter reading back to zero. After the plunger has been in intimate contact with the sample for 15 seconds and the plunger and sample holder have again been touched with the ground wire, the latch is released and the plunger quickly rises and breaks contact with the sample. The plunger charge is +, whereas that on the rubber is negative. This can easily be checked by a proof plane and V.T.V.M. In fact, all of the stocks tested to date have shown a negative charge relative to the mirror surfaced metal plunger. The plunger is then discharged or brought to ground potential by touching it with the ground wire, which immediately produces an additional increase in meter reading because of the absorption of electrons from the ground by the plunger. This final steady meter reading is recorded as the contact potential. While this reading is, of course, not the actual potential on the sample, it is nevertheless directly proportional to the actual potential. The actual potential is probably very high, in the 10,000-volt range, as indicated by the Braun type instrument. The sample holder is touched with the grounded wire, and this discharges the sample holder and brings the meter needle back to zero. This test procedure is repeated five times and the results are averaged. Tests on duplicate samples should always be run and the results averaged. The charge tends to build up to a certain extent in some stocks so that the latter readings are somewhat higher than the initial ones.

All tests should be conducted in a constant-temperature, constant-humidity room maintained at 78° F., and not over 50 per cent relative humidity. High humidity causes erratic results in electrostatic work just as it does in resistivity, dielectric constant, and power factor tests, only to a greater extent.

#### EXPERIMENTAL DATA

As has been previously intimated, our electrostatic contact potential theory of reinforcement is based on the assumption that rubber and GR-S, which

are at the negative end of the electrostatic series, should be reinforced by those materials which are on the positive (less negative) end of the series, and that the more positive or the greater difference in potential between the rubber and reinforcing material, the greater the reinforcement. The converse should also hold true if materials could be found which are highly negative to rubber. This would establish a high contact potential difference which should also give rise to reinforcement.

#### GR-S DATA

To test this theory, one of the most positive materials we had available was milled into a high zinc-oxide loaded GR-S compound and the stock tested for tensile properties and contact potential. From the results of a previous electrostatic investigation, polymerized trimethyldihydroquinoline, an organic resin, was found to be one of the most positive materials, and fifteen parts of it were milled into the stock. A control was also run in which the organic resin was omitted. The tensile results indicated that a 75 per cent increase in tensile strength and an acceleration of vulcanization were obtained by the use of this positive material, and the electrostatic contact potential data showed that the stock was highly positive (less negative) than before it was added. These preliminary results confirmed our theory. Further experiments were then carried out in a carbon black stock, a pure-gum stock, and another zinc oxide stock. The zinc oxide used in this and all subsequent tests was a fine particle size (0.2-micron average diameter), fast-curing type produced by the St. Joe electrothermic process. The results are shown in Table I, and indicate a definite relationship between tensile strength and contact potential. For these and all subsequent tests Flectol-H, an acetone-aniline condensation product, which is also a highly positive resin and is easy to incorporate in rubber, was used. Previous investigators in electrostatics<sup>6</sup> have stressed the importance of dielectric constant, power factor, and resistivity data; these, along with some other physical tests, are included.

#### DIELECTRIC CONSTANT AND POWER FACTOR TESTS

These data were obtained on a series resistance bridge with Wagner ground, using a 1000-cycle oscillator and three-stage electronic eye null indicator<sup>7</sup>.

#### RESISTIVITY DATA

The resistivity tests were run on the St. Joe megohm bridge, using Aquadag electrodes, as suggested by Liska<sup>8</sup>. A photograph and schematic diagram of the St. Joe megohm bridge with built-in vacuum-tube null indicator and 180-volt d.c. voltage regulated power supply are shown in Figures 1 and 2.

It will be observed on examination of the data in Table I that there are notable exceptions to Coehn's rule<sup>8</sup>, which states that the charge is a function of the dielectric constant and that a material is positive to another if it has a higher dielectric constant. There also appears to be no definite relationship between resistivity and contact potential.

Rebound data were obtained with the St. Joe inclined-plane falling-ball rebound tester<sup>9</sup>. The results indicate that while the positive resin decreases the rebound at room temperature, it actually increases it above the regular compound in some cases at 100° C.

TABLE I  
ELECTROSTATIC CONTACT POTENTIALS OF GR-S COMPOUNDS

Formula	Composition	Optimum cure (min.)	*Elec- trostatic contact (potential)	Tensile strength (kg. per sq. cm.)	Elon- gation (%)	Modulus at 400% (kg. per sq. cm.)	Rebound (%) 25.0° C	Rebound (%) 100° C	Di- electric constant	Power factor (%)	Resistivity (d.c.) Ohm cm.	Hard- ness (Shore) (30 sec.)
A	Tread with (+resin)	75 @ 145° C	-1.3	203.9	700	75.6	26.3	31.8	8.6	17	$2.4 \times 10^{10}$	47
	Tread	90 @ 145° C	-2.1	196.9	525	137.1	31.8	38.1	34.6	73	$8.9 \times 10^7$	50
	Zinc oxide with (+resin)	15 @ 137.8° C	-4.0	121.3	800	19.3	32.0	42.8	4.4	1.15	$1.6 \times 10^{14}$	41
	High zinc oxide	45 @ 137.8° C	-5.0	70.3	1050	7.0	35.1	35.7	4.3	.43	$2.8 \times 10^{14}$	31
B	Pure gum with (+resin)	10 @ 137.8° C	-6.0	31.6	600	17.6	38.5	48.0	2.75	1.20	$1.7 \times 10^{14}$	32
	Pure gum	25 @ 137.8° C	-8.0	14.1	725	3.5	43.1	42.2	2.60	.32	$2.0 \times 10^{14}$	25
Formulas												
A												
GR-S	Carbon black (E.P.C.)	100	GR-S			100						
Sulfur		50	Sulfur			2.5					100	
Mercaptobenzothiazole		1.5	Mercaptobenzothiazole			1.5					2.5	
Bardol		1.5	Zinc oxide			5.0					1.5	
Zinc oxide		5.0	Stearic acid			2.5					5.0	
Positive resin		5.0	Zinc oxide			113.0					2.5	
		0 -15	Positive resin			0 -15					0 -15	
											111.5	
		163.0				224.5						
C												
			GR-S									
			Sulfur									
			Mercaptobenzothiazole									
			Zinc oxide									
			Stearic acid									
			Positive resin									

\* For all tables and graphs the electrostatic contact potential readings divided by 10 equals the actual input volts to the amplifier.

## EFFECT OF VULCANIZATION OF GR-S ON CONTACT POTENTIAL

The effect of vulcanization on contact potential and tensile strength is shown in Table II and Figure 9. It will be noted that the cure curves and the contact potential curves are of a similar shape.

TABLE II

EFFECT OF VULCANIZATION ON ELECTROSTATIC CONTACT POTENTIALS OF GR-S STOCKS

Cure (minutes at 137.8° C)	Electrostatic contact potential	Tensile strength (kg. per sq. cm.)	Elonga- tion (%)	Modulus at 400% (kg. per sq. cm.)	Remarks
0	-9.0	Less than 14	—	—	Too soft to test
1	-8.5	Less than 14	—	—	Too soft to test
15	-8.0	Less than 14	—	—	Too soft to test
30	-7.4	22.9	1325	0.7	
45	-4.3	70.3	1075	5.9	
60	-4.5	70.3	950	10.6	
120	-5.5	35.2	550	19.3	

## Formula

	Parts by weight
GR-S	100
Sulfur	2.5
Mercaptobenzothiazole	1.5
Zinc oxide	5.0
Stearic acid	2.5
Zinc oxide	113.0 (20 volumes)
	224.5

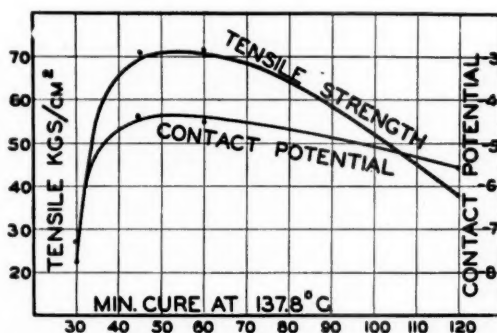


FIG. 9.—Rate of cure and electrostatic contact potential curves.

The results on GR-S indicate that, while there is no definite relationship between dielectric constant, resistivity, and contact potential, there does appear to be some correlation of tensile strength or reinforcement and contact potential. This checks our theory.

## DATA ON RUBBER COMPOUNDS

If the theory is any good, the highly positive resin should also increase the tensile strength not only of GR-S stocks but also of rubber compounds. These data are shown in Table III.



The fact that the carbon black stock is not reinforced by the positive resin would be expected, as it does not make the contact potential appreciably more positive; and furthermore, the carbon black charge is probably in the same potential range, while in the rubber, as the resin charge.

#### HIGH TENSILE PURE-GUM TYPE OF GR-S STOCKS

Since the high-gum type of GR-S stocks has not as yet been produced, it was thought that if a large amount of the positive resin were added to the gum stock, high-tensile stocks should result. Table IV gives the electrostatic

TABLE IV  
HIGH TENSILE PURE-GUM TYPE OF GR-S COMPOUND

Cure (min. at 137.8° C)	30 parts of (+ resin) added Formula G			No (+ resin) added Formula H		
	Tensile strength (kg. per sq. cm.)	Elonga- tion (%)	Modulus at 400% (kg. per sq. cm.)	Tensile strength (kg. per sq. cm.)	Elonga- tion (%)	Modulus at 400% (kg. per sq. cm.)
10	75.3	705	21.1	7.0	700	0.7
15	77.3	700	21.1	14.1	650	3.5
25	65.2	450	33.4	14.1	425	5.3
40	57.5	425	32.5	13.0	300	6.7
Electrostatic contact			Formula G	Formula H		
Potential cure 15 min. $\times$ 280° F			-4.5	-8.0		
Formulas			G	H		
GR-S			100	100		
Sulfur			2.5	2.5		
Mercaptobenzothiazole			1.5	1.5		
Zinc oxide			5.0	5.0		
Stearic acid			2.5	2.5		
(+resin)			30.0	0.0		
			141.5	111.5		

contact potential and tensile data on a stock containing 30 parts of the positive resin. It will be noted that the resin has made the stock more positive (less negative) and has increased the tensile strength from 14 to 77 kg. per sq. cm.

#### APPLICATION OF THEORY TO PIGMENTS IN GR-S

While we have been unable to measure the contact potential of pigments such as carbon black and zinc oxide, if the theory is correct, we would expect these materials, when added to rubber, to produce a stock having a more positive (less negative charge). By checking over the results already given for GR-S and rubber on carbon black and zinc oxide stocks (Table I to III), it will be observed that the theory holds good even for pigments. As a further check, the results on several other stocks containing various pigments are shown in Table V. These data on clay, whiting, and blanc fixe again indicate the relationship between contact potential and reinforcement.

In Figure 10 all of the contact potential data on GR-S have been plotted against the tensile strength of the resulting compounds. It appears that there is a relationship between tensile and contact potential.

In Figure 11 all of the contact potential data on rubber have been plotted against the tensile strength of the resulting compounds. Here again there



TABLE V  
EFFECT OF VARIOUS PIGMENTS IN GR-S COMPOUNDS ON THE ELECTROSTATIC CONTACT POTENTIAL

Pigment	Optimum cure (min. at 145° C)	Elec-trostatic contact (potential)	Tensile strength (kg. per sq. cm.)	Elongation (%)	Modulus at 400% (kg. per sq. cm.)	Rebound (%) 25.6° C	Dielectric constant (K)	Power factor (%)	Resistivity (d.c. ohm cm.)	Hardness (Shore) (30 sec.)
Suprex clay (hard clay)	60	-4.0	103.7	793	21.1	34.9	3.72	1.8	$1.6 \times 10^{14}$	45
Blanc fixe	20	-5.5	56.3	918	5.3	34.6	3.48	.29	$1.6 \times 10^{14}$	36
Calcene (CaCO <sub>3</sub> )	20	-6.0	55.0	675	19.3	32.9	3.25	.5	$1.1 \times 10^{14}$	42
Whiting (dry ground)	20	-7.5	17.6	1000	—	36.8	3.26	.29	$1.6 \times 10^{14}$	29

Base formula

Parts by wt.

100

GR-S

Sulfur

2.5

Mercaptobenzothiazole

1.5

Zinc oxide

5.0

Stearic acid

2.5

Pigment added

30 volumes

Pigment added to base formula  
Suprex clay 78  
Blanc fixe 128  
Calcene 81.3  
Whiting 81.3

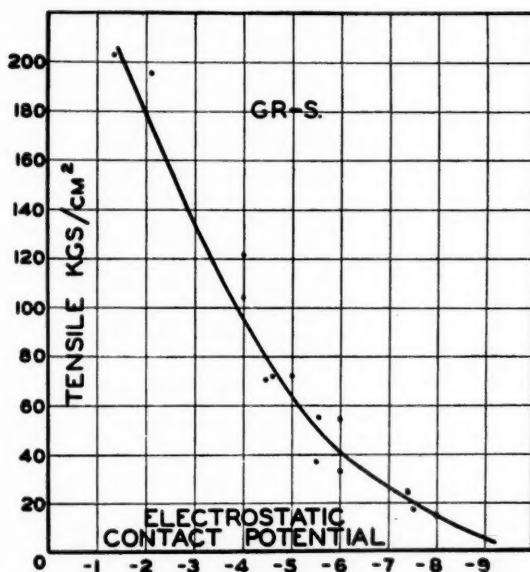


FIG. 10.—Contact potential against tensile strength for all GR-S compounds.

appears to be a relationship. However, it is a different one from that of GR-S, as might be expected from the difference in physical and chemical properties of the two materials. The fact that the rubber is positive to GR-S accounts only partly for the higher tensile strength of the rubber compounds, while the fact that the GR-S is negative to rubber accounts in part for its lower tensile strength and also for the fact that it can be reinforced a greater percentage than rubber by the same materials which reinforce rubber.

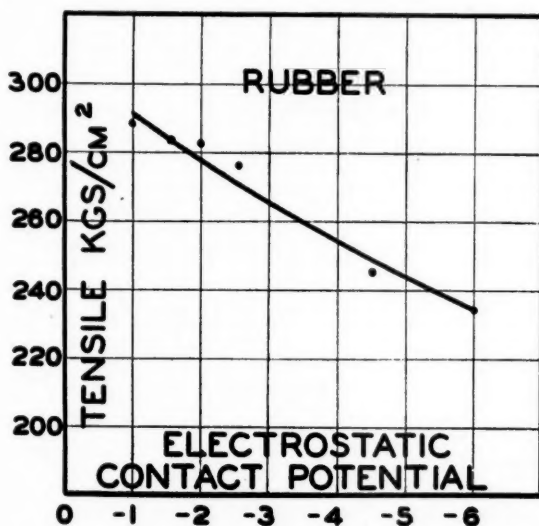


FIG. 11.—Contact potential against tensile strength for all rubber compounds.

## SUMMARY AND CONCLUSIONS

A new electrostatic modulator has been described for measuring the electrostatic charges on rubber, synthetic rubber, and various materials. In this apparatus the electrostatic lines of force established between the charged specimen and a stationary electrode plate connected to the grid of an audio-frequency amplifier are cut or modulated at audiofrequency by a small four-bladed, motor-driven fan. This produces in effect an alternating current voltage which can be readily amplified by the audio amplifier and quantitatively measured on a meter in the output circuit.

This device, in conjunction with a mirror-surfaced metal plunger system for contacting the rubber samples, has been used to measure the contact potential of various rubber and GR-S compounds.

Electrostatic contact potential data are shown for both rubber and GR-S compounds with and without organic and inorganic reinforcing agents, and these data bear out the formulation of an electrostatic contact potential theory of reinforcement in which the reinforcement of rubber and GR-S is explained on the basis of contact potentials and resultant electrostatic attractive forces which exist between the rubber and the reinforcing agents.

By the application of this theory, organic materials which have a highly positive electrostatic charge, such as polymerized trimethyldihydroquinoline and Flectol-H (an acetone-aniline condensation product), have been found to increase the tensile strength of the pure-gum type of GR-S compounds as much as fivefold and nearly to double the tensile strength of high zinc oxide loaded GR-S compounds.

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# SOME RELATIONS BETWEEN STRESS, STRAIN, AND TEMPERATURE IN A PURE-GUM VULCANIZATE OF GR-S SYNTHETIC RUBBER\*

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## INTRODUCTION

Some relations between stress, strain and temperature have been investigated for a pure-gum vulcanizate of GR-S to furnish experimental information for use in theoretical consideration of its elastic behavior. The results of the work also yield some practical information about the tensile properties at high and low temperatures.

In this work stress was studied as a function of temperature, with the elongation, or sometimes the length, constant. In this way effects of friction and flow accompanying changes in length of specimens were minimized.

The general methods employed in this study were first outlined by Meyer and Ferri<sup>1</sup>, who in common with other observers<sup>2</sup> applied them to natural rubber. Peterson, Anthony, and Guth<sup>3</sup>, in the only studies of this sort dealing with synthetic rubber, did not include GR-S or other butadienestyrene copolymers.

## EXPERIMENTAL PROCEDURE

### COMPOUND AND CURE

The compound was prepared according to the following recipe:

	Parts by weight
GR-S	100
Sulfur	2
Zinc oxide	1
Zinc dibutyldithiocarbamate	0.5
Total weight of compound	103.5

This recipe was selected because it seemed to involve the addition of about a minimum quantity of compounding ingredients to raw GR-S to produce a well-vulcanized product. The GR-S employed for part of this investigation was received in January, 1943 from the Rubber Reserve Company plant operated by the Goodyear Company in Akron, Ohio. GR-S employed for the remainder of this investigation was prepared for the Office of the Rubber Director and labeled ORD No. 45. The compounds were vulcanized in the form of sheets, of which some were about 0.065 inch thick, others about 0.080 inch thick. The curing conditions were chosen to give vulcanizates of approximately maximum stiffness. At 292° F this required 35 minutes and 25 minutes, respectively, for the Goodyear GR-S and ORD No. 45.

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## SPECIMENS

The GR-S specimens were in the form of flat strips or dumbbells 0.5 inch wide and measuring 2 inches, 10 centimeters, or sometimes 20 centimeters, between gauge marks. They were stretched by dead-weight loading with manual control of the elongation, which could be observed by means of replaceable fiducial marks and a graduated scale viewed through a glass window.

The specimens, fiducial marks, and scale were contained in an enclosure through which a vigorous current of air was circulated by a blower. The air was heated by resistance coils of the type used in radiant heaters or cooled by the use of dry ice. Consequently at the lower temperatures the specimens were surrounded by an atmosphere containing large amounts of carbon dioxide. No effects ascribable to the carbon dioxide were noted.

## DEFINITIONS OF CONSTANT ELONGATION AND STRESS

Stress-temperature studies on the Goodyear GR-S were all made with the specimens held at constant elongation. Studies on the ORD No. 45 were made both for constant length and for constant elongation.

For the portion of the work in which the elongation was kept constant, the percentage elongation was always measured with reference to the unstretched length at that particular temperature. In other words, as the temperature was varied, the distance between gauge marks was not held constant, but was kept proportional to the unstretched length at each temperature. Consequently the elongation, as just defined, was maintained constant as the temperature was varied. To obtain this constant elongation, the distance between the gauge marks on an unstretched specimen was measured over the whole range of temperatures studied so that all elongations could be referred to the corresponding unstretched lengths at each temperature. There was moderately good agreement between the measured unstretched lengths and those calculated by the use of the linear expansivity,  $220 \times 10^{-6}$  per  $^{\circ}\text{C}$ , commonly employed in this laboratory for pure-gum vulcanizates of natural rubber.

The stress is defined for the purposes of the present work, in accordance with the usual practice, as the force per unit area of original cross-section (the area being measured at room temperature).

## RELAXATION OF STRESS

To minimize the effects of relaxation of stress during the observations of stress-temperature relations, the specimens were first stretched to the desired elongation and held at a constant temperature for a period of 0.5 hour to 2 hours. It was found that after this treatment no further relaxation occurred during the stress-temperature studies.

## STRESS-TEMPERATURE RELATIONS

The stress-temperature relations were investigated only for temperatures below the temperature at which the relaxation occurred. The temperature was lowered by steps to the neighborhood of  $-20^{\circ}\text{C}$ , and the loads were reduced so as to maintain constant elongation or constant length. Finally the temperature was again raised and the load increased. When the increase of temperature yielded the same values of stress which had been obtained with decreasing temperatures, it was concluded that no appreciable relaxation or flow had occurred during the cycle of temperature variation.

## SET

At the conclusion of a stress-temperature cycle the load was removed, and the distance between the gauge marks was measured with a magnifying glass and a steel scale graduated in hundredths of an inch. When the increase in the distance over that measured at the beginning of the experiment was greater than 0.2 per cent, the specimen was discarded after a determination of its permanent set. The term permanent set is used in this paper as a measure of the percentage increase in length of the unstretched specimen which remains after it had been heated in the unstretched state to about 100° C for a few minutes and then stored for one or two days at room temperature. When the initial set was less than 0.2 per cent it was considered negligible, and the specimen was sometimes used for further experiments.

## RESULTS

## RELAXATION OF STRESS

The relaxation of stress with time, observed at constant temperatures, is shown for elongations of 10 per cent and 50 per cent in Figures 1 and 2, re-

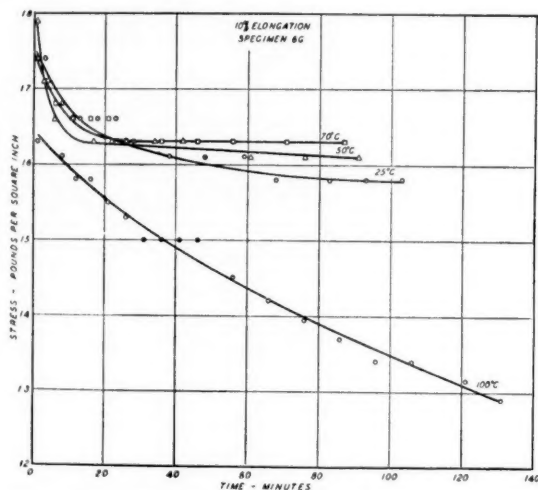


Fig. 1.—Stress-time relations for an elongation of 10 per cent. The tests were conducted in the order of increasing temperature.

spectively. It will be noted that, for temperatures of 25°, 50°, and 70° C, the rate of decrease of stress becomes relatively small after about 20 minutes, and approaches a more or less constant or equilibrium value. At 100° C, however, the rate did not decrease appreciably, even after two hours. Relaxations at this temperature were also accompanied by large permanent set, which is an indication of flow. The exactness of approach of the stresses to an equilibrium at temperatures of 70° C and below was not investigated for times longer than about two hours, since the only aim was to have no appreciable further change with time during observations of stress-temperature relations.

The values of stresses observed after relaxation at various elongations and temperatures are listed in Table I, and are used to plot the stress-strain curve



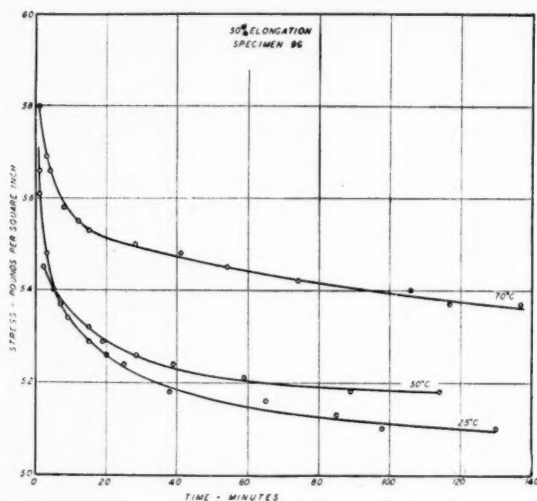


Fig. 2.—Stress-time relations for an elongation of 50 per cent. The tests were conducted in the order of increasing temperature.

shown in the upper part of Figure 6. In this figure the stresses after relaxation at 20° and 30° C may, for all practical purposes, be considered the same as if the relaxations had occurred at 25° C. The stresses after relaxation at 70° C are only slightly higher than those for 25° C. Inasmuch as the stresses at 50° C lie between those of 25° and those at 70° C, they are not shown on the graph. However, at 70° C the specimens broke during the relaxation period when the elongation was greater than 50 per cent.

TABLE I  
RESULTS OF STRESS-TEMPERATURE STUDIES AFTER RELAXATION AT  
CONSTANT ELONGATION

Specimen number	Elongation (%)	Temperature of relaxation (° C)	Stress at temperature of relaxation (lb. in. <sup>-2</sup> )	Values from stress-temperature curves for constant elongation	
				Slope (lb. in. <sup>-2</sup> deg. <sup>-1</sup> )	Intercept at 0° K (lb. in. <sup>-2</sup> )
6G	10	25	15.8	0.071	- 6.4
7G	20	25	27.1	0.104	- 3.9
2G	35	25	39.9	0.164	- 9.0
9G	50	25	51.0	0.191	- 5.9
10G	75	25	65.8	0.268	-14.1
6F	100	30	74.8	0.296	-14.9
3E	125	25	85.0	0.366	-24.1
8D	150	20	90.5	0.414	-30.8
10F	150	20	95.7	0.412	-25.0
6G	10	50	16.1	0.065	- 4.9
7G	20	50	28.0	0.096	- 3.0
8G	35	50	41.4	0.149	- 6.7
9G	50	50	51.7	0.180	- 6.4
8F	75	40	65.2	0.255	-14.6
6G	10	70	16.3	0.057	- 3.3
4F	20	70	28.3	0.093	- 3.6
8G	35	70	42.8	0.140	- 5.2
9G	50	70	53.7	0.174	- 6.0

## STRESS-TEMPERATURE RELATIONS

Typical results of stress-temperature relations in which the elongation was held constant are shown in Figures 3 and 4. The data represented by the uppermost curves in Figures 3 and 4 were obtained after carrying out the

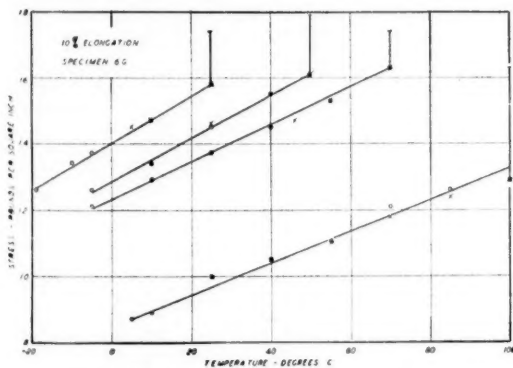


FIG. 3.—Stress-temperature relations for an elongation of 10 per cent. Each stress-temperature relation was obtained after the corresponding relaxation shown in Figure 1. The vertical line at the point of the highest temperature shows the amount of relaxation and the temperature at which it occurred.

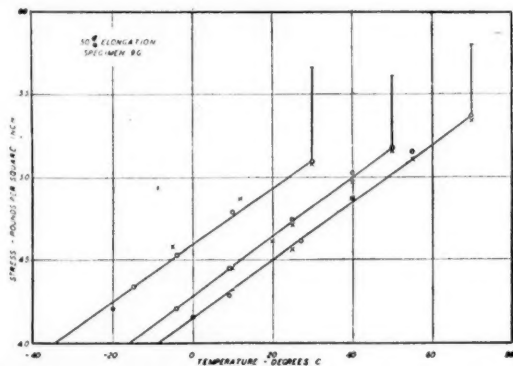


FIG. 4.—Stress-temperature relations for an elongation of 50 per cent. Each stress-temperature relation was obtained after the corresponding relaxation shown in Figure 2. The vertical line at the point of the highest temperature shows the amount of relaxation and the temperature at which it occurred.

relaxation at 25° C shown in Figures 1 and 2, respectively. The vertical lines at the upper end of each curve represent the decrease in stress during the relaxation. Stresses obtained as the temperature was lowered are represented by circles on the graph. Stresses observed as the temperature was increased are shown by crosses. The second and third curves in Figures 3 and 4 were obtained in a similar manner after relaxations at 50° and 70° C, respectively. The fourth curve in Figure 3 was obtained after the relaxation at 100° C shown in Figure 1. The value of permanent set at the conclusion of this experiment was about 2 per cent, whereas the values after similar experiments at 70° C were of the order of 0.5 per cent. No further experiments were conducted at 100° C.

A linear relation between stress and temperature was invariably obtained. Repeated cycles of variation of temperature produced the same values of stress.

Within the limits of observation the stress was now found to be no longer a function of time but to depend solely on the elongation, the temperature, and the temperature at which the relaxation had occurred. If the temperature was raised above that at which relaxation had occurred, straight lines were not obtained, since further relaxation occurred at these higher temperatures, and the stress became again dependent on the time. After relaxation the straight lines could be obtained as before by lowering the temperature. It can be noted from Figures 3 and 4 that the value of the stress at a given temperature and the slope of the stress-temperature lines depend on the temperature at which the relaxation occurred.

The same stress-temperature lines were obtained after relaxation at 70° C, regardless of whether or not relaxation at 25° C had occurred previously. However, after relaxation at 70° C a recovery period during which the rubber remained unstretched was required before the values corresponding to the original relaxation at 25° C could be again obtained. This recovery period was of the order of days at room temperature, but could be very considerably reduced if the unstretched rubber were heated above room temperature. In the following work, however, when data for different relaxation temperatures are reported for the same specimen, the data for the lower relaxation temperatures were always observed first.

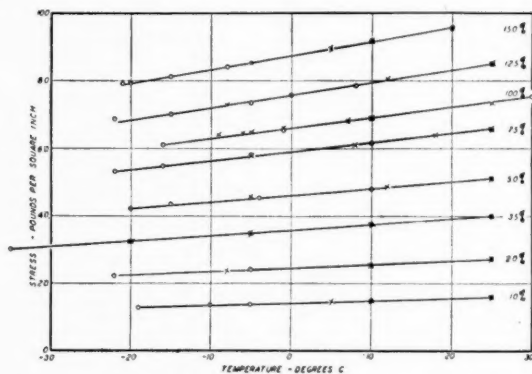


FIG. 5.—Stress-temperature relations for various elongations. With two exceptions the relaxation temperature was 25° C. At 100 per cent elongation it was 30° C and at 150 per cent it was 20° C.

Figure 5 shows stress-temperature relations for various elongations. Except for two of the curves shown, the relaxations were conducted at 25° C. Difficulty in finding a specimen which would not fail at 150 per cent elongation during the relaxation at 25° C led to the use of a relaxation temperature of 20° C for this elongation. The relaxation at 100 per cent elongation was carried out at 30° C.

It will be noted that the slopes of the lines representing the stress-temperature relations are greater at the higher elongations. When the lines were extrapolated to 0° K, they were observed to have negative intercepts on the stress axis. These intercepts are shown graphically in the lower portion of Figure 6. The extrapolation is carried out for the purpose of furnishing data for theoretical calculations and, of course, in no way assumes that the actual stress-temperature relation is linear for GR-S at temperatures below those which were investigated.

From our definition of constant elongation it follows that the curve representing the stress-temperature intercepts should pass through zero at zero elongation. This conclusion is evident when we note that for a constant elongation equal to zero the stress should always be zero. The corresponding stress-temperature graph then coincides with the temperature axis, and its intercept, of course, is zero. The intercept curve in Figure 6 is drawn through the origin and is a straight line. This line seems to represent the data within the experimental errors.

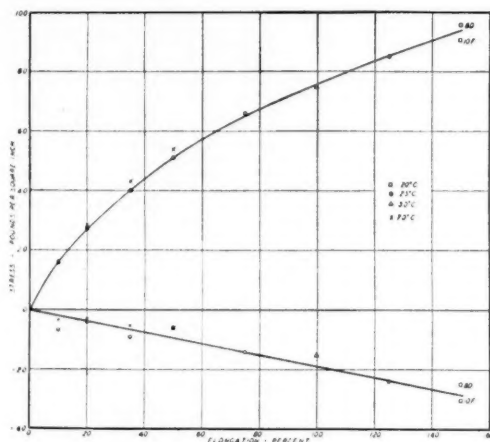


Fig. 6.—Stress-elongation relations (upper curve) and stress-temperature intercepts at  $0^{\circ}$  K (lower curve). The data were observed after periods of relaxation from 0.5 hour to 2 hours at constant elongation.

Table I presents for various elongations and for various relaxation temperatures the values of stresses after relaxation, the slopes of the stress-temperature lines, and their intercepts. It can be seen from this table that the stresses after relaxation increase somewhat with increasing temperature, and the slopes of the stress-temperature lines decrease with increasing temperature of relaxation. The uncertainty in the results does not warrant any definite conclusions on the effect of temperature on the intercepts.

#### PERMANENT SET

The permanent set for experiments reported in Table I ranged from negligible values to as high as 1.5 per cent. In experiments where the relaxation temperature was  $20^{\circ}$  to  $30^{\circ}$  C, the permanent set was less than 0.5 per cent for elongations up to 75 per cent. The set was about 1 per cent for 100 per cent elongation, and became somewhat greater for higher elongations. Where the relaxation temperature was  $40^{\circ}$  or  $50^{\circ}$  C, the set ranged from less than 0.5 to 1 per cent. Where the relaxation temperature was  $70^{\circ}$  C, the set became as great as 1.5 per cent at an elongation of 50 per cent.

#### EQUILIBRIUM STRESS-STRAIN CURVES

It has been pointed out that during the relaxation of stress at constant elongation and constant temperature the stress decreases, approaching fairly near to constancy after a period ranging from 0.5 hour to 2 hours. In these

experiments the specimens had not been stretched previously to an elongation greater than that under study. In a few additional experiments, however, the change of stress with time was investigated after the specimen had been maintained for some time at a greater elongation. The stress was found to be considerably lower at first than the lowest value attained in the previous experiments, but it now increased with time and approached the same final value. No detailed investigation of this effect was made to determine the effects of extended periods of relaxation. However, since the value of the stress after relaxation may be approached from either direction, it will be regarded for the purposes of this paper as an equilibrium value. The curve obtained when such values are plotted against the corresponding elongations is then an "equilibrium" stress-strain curve. The upper curve of Figure 6, plotted from data in Table I, is a typical graph of this sort.

Our studies of various samples of GR-S have shown differences in the stress-strain properties of different specimens, even when they are cut from the same sheet of vulcanizate. This nonuniformity is found to be present also for stresses observed after relaxation, and accounts for some of the variations shown in Figure 6 and Table I, where each value was obtained from a different specimen. To minimize these variations and to obtain an equilibrium stress-strain curve for a single specimen, studies were made for a series of elongations of one specimen. In this study the specimen was first allowed to relax at the lowest elongation to be studied. Then after recording the equilibrium stress the load was increased and the specimen allowed to relax at the next elongation. The data for such a stress-strain curve obtained from a specimen of the ORD No. 45 GR-S are shown in Table II and plotted in the upper part of Figure 7. The

TABLE II  
RESULTS OF STRESS-TEMPERATURE STUDIES ON A SINGLE SPECIMEN.  
THE RELAXATIONS WERE CONDUCTED AT 30° C

Elongation (%)	Stress at 30° C (lb. in. <sup>-2</sup> )	Values from stress-temperature curves			
		Constant length		Constant elongation	
		Slope (lb. in. <sup>-2</sup> deg. <sup>-1</sup> )	Intercept at 0° K (lb. in. <sup>-2</sup> )	Slope (lb. in. <sup>-2</sup> deg. <sup>-1</sup> )	Intercept at 0° K (lb. in. <sup>-2</sup> )
5	8.5				
7.5	12.3				
10	16.0	0.0276	+7.7	0.0685	- 4.7
12.5	18.6				
12.5 <sup>a</sup>	18.6				
15	22.0				
17.5	24.6				
20	27.4	0.0672	+7.0	0.101	- 2.3
25	32.4				
30	37.2				
35	42.1				
35 <sup>a</sup>	41.1	0.130	+1.9	0.158	- 6.7
40	45.1				
45	48.6				
50	52.5	0.172	+0.4	0.20	- 8.1
50 <sup>b</sup>	54.9				
60	60.3				
75	69.4	0.236	-2.3	0.266	-11.4
100	83.2	0.302	-8.1	0.338	-19.1
125	93.5				

<sup>a</sup> Specimen was allowed to relax over night.

<sup>b</sup> Load was removed for 40 hours previous to a relaxation period of 1.5 hours.

points shown in this figure as triangles and squares refer to other specimens. In Table II it will be noted that at elongations of 12.5 per cent and 33 per cent no great change in stress was observed even when the specimen was allowed to relax over night. At 50 per cent elongation the load was removed for 40 hours and a new value of stress was observed and recorded after 1.5 hours of relaxation. At 125 per cent elongation the specimen broke before stress-temperature relations could be observed.

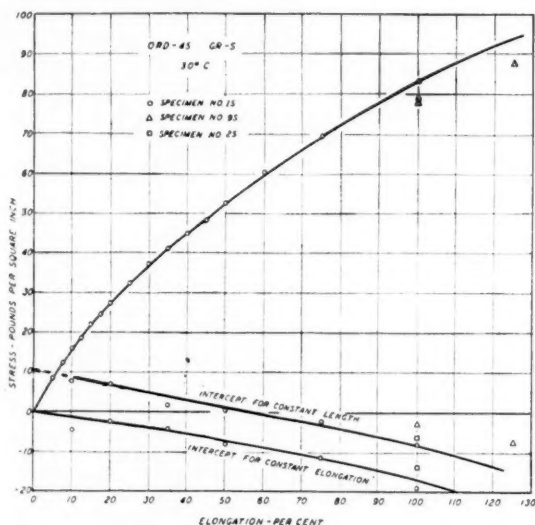


Fig. 7.—Stress-elongation relations and stress-temperature intercepts at  $0^{\circ}$  K. The relaxations were conducted at  $30^{\circ}$  C. After the desired observations at one elongation the specimen was usually stretched to the next higher elongation without removing the load. Except for the points shown as triangles and squares, the data were all obtained from one specimen.

#### STRESS-TEMPERATURE RELATIONS FOR CONSTANT LENGTH AND FOR CONSTANT ELONGATION

Stress-temperature relations were also studied as before except that the process was carried through two cycles of temperature variation. For one cycle the elongation was kept constant as before, and for the other one the length of the specimen was kept constant. The results of an experiment of this kind are also shown in Table II, and the intercepts are plotted in the lower part of Figure 7.

Figure 8 and Table III show similar data observed for a relaxation temperature of  $0^{\circ}$  C. At 50 per cent elongation the load was removed after relaxation and observation of the stress-temperature relation, and the specimen was allowed to rest over night at room temperature. The temperature was again lowered to  $0^{\circ}$  C the next morning, and the specimen was again allowed to relax at 50 per cent elongation. The value shown in Table III was observed after 50 minutes. At 200 per cent elongation the specimen broke during the relaxation. The values for the points shown as triangles at 150 per cent and 175 per cent elongation were observed for another specimen.

At the time that most of the work described in the present paper was performed, it appeared that theoretical interest was largely concerned with stress-temperature relations at constant elongation. Indeed, previous workers<sup>4</sup>, who



had maintained specimens at constant length, introduced corrections to obtain results at constant elongation. However, more recent theoretical interest, as discussed by James and Guth<sup>5</sup>, seems more concerned with stress-temperature relations at constant length. Relatively simple equations can be derived relating the values of slope and intercept obtained by the two methods. The

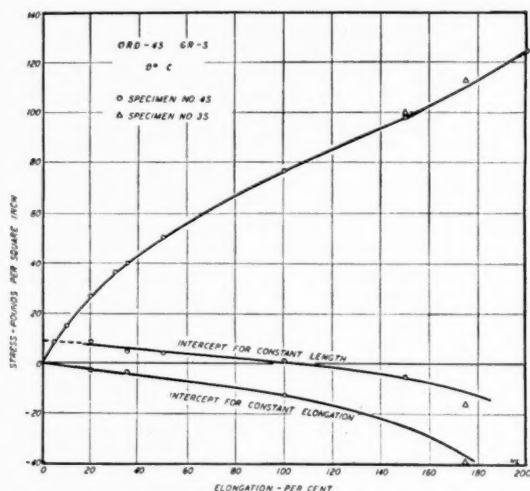


Fig. 8.—Stress-elongation relations and stress-temperature intercepts at 0° K. The relaxations were conducted at 0° C. After the desired observations at one elongation, the specimen was usually stretched to the next higher elongation without removing the load. Except for the points shown as triangles, the data were all obtained from one specimen.

TABLE III  
RESULTS OF STRESS-TEMPERATURE STUDIES ON A SINGLE SPECIMEN.  
THE RELAXATIONS WERE CONDUCTED AT 0° C

Elongation (%)	Stress at 0° C (lb. in. <sup>-2</sup> )	Values from stress-temperature curves			
		Constant length		Constant elongation	
		Slope (lb. in. <sup>-2</sup> deg. <sup>-1</sup> )	Intercept at 0° K (lb. in. <sup>-2</sup> )	Slope (lb. in. <sup>-2</sup> deg. <sup>-1</sup> )	Intercept at 0° K (lb. in. <sup>-2</sup> )
5	8.5				
10	15.2				
20	26.9	0.066	+8.9	0.108	- 2.6
30	36.2				
35	39.9	.127	+5.2	.158	- 3.2
50	50.6	.168	+4.4		
50*	50.9				
100	76.9	.276	+1.5	.328	-12.7
150	98.4	.380	-5.2		
200	125				

\* Load was removed for 17 hours previous to a relaxation period of 50 minutes.

direct experimental comparison of the results obtained on the same specimen by the two methods was made to clarify this point.

The values of the intercepts of stress-temperature curves at constant elongation are negative, and are nearly proportional to the elongation. The numerical values of the intercepts are of the order of 10 per cent of the equilibrium stresses at the lowest elongations, and increase to almost 30 per cent at the

highest elongations. The values of the intercepts of the stress-temperature curves obtained at constant length are positive at the low elongations and negative at the high.

#### NON-EQUILIBRIUM STRESS-STRAIN RELATIONS

Studies were made of the stress-strain relations obtained at  $-20^{\circ}$ ,  $25^{\circ}$  and  $70^{\circ}$  C by elongating the specimen at an average rate of about 200 per cent per minute, and then immediately allowing retraction at the same rate. This rate is between one-quarter and one-half that employed in the usual testing machines. Dead-weight loading was employed in these studies, the stress being varied by increments of about 12.5 lbs. per sq. in. Typical results for a specimen of the Goodyear GR-S are presented in Figure 9. Two cycles of ex-

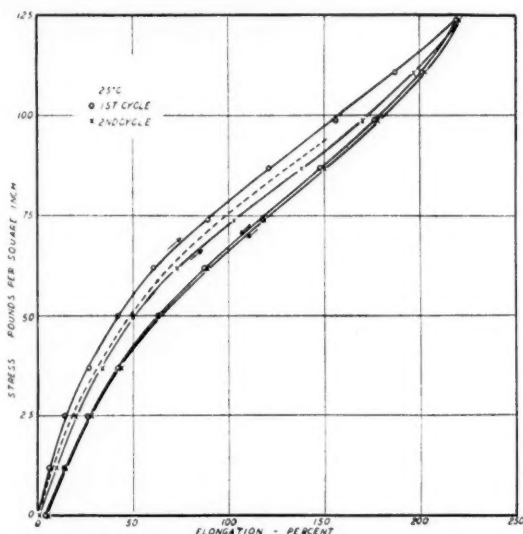


Fig. 9.—Stress-elongation relations for extension and retraction at the rate of about 200 per cent per minute. There was an interval of about 3 minutes between the two cycles. The broken line shows the stress-elongation curve from Figure 6 for comparison.

tension and retraction are shown. The equilibrium stress-strain curve from Figure 6 is shown as a broken line curve for purposes of comparison. The second extension curve in this study is substantially lower than the first extension curve. The retraction curves for the two cycles differ only slightly. As would be expected, the equilibrium curve lies below the first extension curve at all elongations. However, higher elongations and stresses are attainable at this speed of stretch than can be maintained during relaxation. Table IV gives for various temperatures the approximate values of the maximum stress and the maximum elongation which are attainable by the two methods of stretching.

#### DISCUSSION OF RESULTS

##### GENERAL COMPARISON WITH NATURAL RUBBER

The results presented here are similar in many respects to those obtained in this laboratory when similar experiments<sup>6</sup> were conducted with natural

TABLE IV  
MAXIMUM VALUES OF STRESS AND ELONGATION AT VARIOUS TEMPERATURES FOR A  
STRETCHING RATE OF ABOUT 200 PER CENT PER MINUTE, COMPARED  
WITH THE CORRESPONDING VALUES AFTER RELAXATION

Temperature (° C)	Stretched at 200% per minute		After relaxation	
	Maximum elongation (%)	Maximum stress (lb. in. <sup>-2</sup> )	Maximum elongation (%)	Maximum stress (lb. in. <sup>-2</sup> )
-20	560	450	—	—
0	—	—	200	125
25	300	150	150	100
50	—	—	70	65
70	160	110	50	55

rubber. A major difference exists, however, with respect to the phenomena associated with crystallization, which seems to be entirely absent in GR-S and to play a very important part in determining the stress and strain at elongations above 150 per cent in the natural rubber compound. For this reason the results of the present work with GR-S are much simpler than those observed with natural rubber. A considerable portion of the present work was completed before the work on natural rubber was begun, and was useful as a guide in showing which results were associated with crystallization. Reference should be made to the paper<sup>6</sup> on natural rubber for a description of the effects of crystallization on the properties under investigation. None of them was ever observed in any of the experiments on GR-S.

#### TEMPERATURE OF RELAXATION

It will be observed from Figure 1 that at 100° C the stress continues to decrease, the rate of decrease becoming approximately constant. The stress does not approach an equilibrium value, as it does at the lower temperatures.

At a temperature of 70° C and below, it can be seen that this effect is not appreciable, at least during the time of the observations. On the basis of these experiments no further work was done at 100° C, since it was desired to avoid effects connected with oxidation. It may be concluded that the temperature at which this becomes appreciable in a few hours is between 70° and 100° C. In natural rubber the corresponding temperature was found to lie between 25° C and 70° C. Much more complete studies of this effect have been made recently by Tobolsky, Prettyman, and Dillon<sup>7</sup>, whose experiments were conducted largely at 100° C and higher temperatures. They have shown that the stress at these temperatures ultimately becomes zero, and have presented convincing evidence that the effect is caused by oxidative scission of the long chain molecules. A theoretical discussion of the causes of relaxation in rubber has been given recently by Mooney, Wolstenholme, and Villars<sup>8</sup>.

#### STRESS RELATIONS

The stress may be regarded as a quantity which depends on the elongation, the temperature, and the previous thermal and mechanical history of the specimen. A brief summary of the results already given will serve to indicate, in a more unified presentation, the nature of this dependence. An effort will be made to present the general features as clearly as possible, even at the risk of possible slight inaccuracies arising from second-order effects such as flow or oxidation. The upper limit of temperature in the discussion is taken as 70° C and the lower limit as -20° C.

At temperature  $T$  and elongation  $E$  there is a corresponding stress value  $S_E$  representing an equilibrium condition. The actual value  $S$  of the stress at a given time may not equal the equilibrium value  $S_E$  because of the previous thermal or mechanical history of the specimen. At room temperatures and above, the stress in the pure-gum GR-S compound studied attains a value within a few per cent of  $S_E$  in less than two hours after application of the load. Thereafter there are no further changes with time, provided that the elongation is unaltered and provided that the temperature is not raised above that at which the relaxation occurred. No time effects are introduced by lowering the temperature and then raising it to the relaxation temperature, or by repeating the variation a number of times. The stress-temperature relation under these conditions is linear.

There are evidently two factors which have opposite effects on the stress at constant elongation as the temperature is raised above the relaxation temperature. The one is an increase, in accordance with the positive slope of the stress-temperature relation already discussed; the other is a decrease corresponding to the additional relaxation which occurs at the higher temperature. The two factors nearly counterbalance each other as far as the equilibrium stress at different temperatures is concerned. A slight predominance of the former factor is responsible for the small increase of equilibrium stress with temperature. When the temperature is decreased after relaxation, the stress is affected by only the first factor. As the temperature is increased, the second factor comes into effect only at temperatures above the relaxation temperature. The second factor is time-dependent, but becomes approximately constant in a period of the order of hours. The first factor is not time-dependent.

It is evident that measurements of stress-strain isothermals at two different temperatures cannot be used for calculation of the stress-temperature relation at constant elongation, since the changes shown by the isothermals reflect only the difference of the two factors.

A previous heating of the unstretched rubber appears to have no influence, but if the stretched specimen has been heated to a temperature higher than  $T$ , or if it has been stretched to a greater elongation than  $E$ , and the new condition maintained for a sufficient time, the stress will be found to be temporarily less than  $S_E$ .

It is clear that immediately after any stretching for the first time the stress will be greater than  $S_E$ . The first extension curve in Figure 9 shows higher stresses than  $S_E$  at all elongations. The retraction curves in Figure 9 lie below the  $S_E$  curve, but would not have done so if the maximum elongation had been sufficiently small and the rate of elongation sufficiently rapid. The second extension curve, as shown in Figure 9, is so influenced by the maximum extension and rate of stretch in the first cycle that its position relative to the equilibrium curve cannot be predicted. It is invariably below the first extension curve.

When the load is completely removed from a stretched specimen,  $S$  is reduced to zero. This is, of course, less than the  $S_E$  corresponding to the residual elongation. Almost all the residual elongation disappears in time under the constant stress of zero because of the influence of the same factors that, at constant elongation, bring about the increase of  $S$  to the corresponding  $S_E$  after a reduction of elongation.

The values of equilibrium stress are relatively little influenced by temperature. However, the maximum stress and strain are very much affected by temperature, as is evident from Table IV. Consequently, investigations in

which relaxation is carried out at low temperatures offer an obvious means of investigating the nature of the equilibrium stress-strain curve at higher elongations than are possible at room temperature.

#### APPLICATION OF RESULTS

Predictions of the tensile properties of GR-S under different conditions of elongation and at different temperatures may be made by a careful consideration of the phenomena described in the preceding section. Furthermore, results obtained from stress-temperature studies can be utilized, with the aid of thermodynamic equations of the type discussed by Gerke<sup>9</sup>, in evaluating the relative effects of energy and entropy in determining the elastic properties of GR-S. Such a utilization, with the necessary qualifications, is beyond the scope of the present paper, which aims to present only experimental results.

The stress relations just described appear to us to be the fundamental ones associated with the elasticity of any rubberlike material. In natural rubber they are evident at low elongations, but are masked to a certain extent at higher elongations by superposed effects caused by crystallization. A synthetic rubber like GR-S which is free from crystallization offers a particularly favorable medium for studying these effects in their simplest form.

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# STRESS-TEMPERATURE RELATIONS IN A PURE-GUM VULCANIZATE OF NATURAL RUBBER\*

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## INTRODUCTION

The stress-temperature relations found in natural rubber are of considerable importance in understanding its elastic behavior. Studying stress as a function of temperature makes it possible to conduct experiments in such a way that there is a minimum amount of relative movement of the different portions of the rubber during the course of the observations. The results of studies made in this way are less influenced by effects arising from friction and flow than are those in which there is relative movement.

In the course of the present investigation the stress-temperature relations for a pure-gum vulcanizate of natural rubber were investigated under conditions of constant elongation. The upper limit of elongations was set by the breaking of the specimen between 700 and 800 per cent. The limits of temperature were from 70° C to about -10° C. As incidental parts of the investigation the following results were obtained: (1) intercepts for the stress-temperature relations at 0° K; (2) stress relaxation in the rubber during the first few hours after stretching; and (3) stress-strain relations after such relaxation. The stress-strain relations may be considered as approaching equilibrium values for elongations up to about 150 per cent, since nearly the same values are obtained following extension or retraction.

The crystallization of the rubber which occurs on stretching and which may continue to increase after stretching has been found to be a factor of very considerable importance in the explanation of the results obtained. In the particular compound studied, no effects ascribable to crystallization were observed at 25° C at elongations below 150 per cent. At elongations above 500 per cent the crystallization which occurs during stretching and in the first few minutes thereafter is apparently so complete that no later changes associated with continued crystallization are noted. At elongations between 150 per cent and 500 per cent crystallization continues for hours after stretching.

## EXPERIMENTAL PROCEDURE

### COMPOUND AND SPECIMENS

The compound studied was as follows:

	<i>Parts by weight</i>
Smoked sheet (natural rubber)	100
Sulfur	2
Zinc oxide	1
Zinc dibutyldithiocarbamate	0.5
	<hr/> 103.5

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It was vulcanized for 40 minutes at 10 lbs. per sq. in. steam pressure. The time selected was that which gave a vulcanizate of maximum stiffness. This particular compound was chosen because it seems to involve the addition of about a minimum quantity of compounding ingredients to the raw rubber to produce a well-vulcanized product. The addition of an antioxidant in the compound would have produced a vulcanizate which would have remained somewhat more stable for long periods of storage, and would have been subject to somewhat less flow at high temperatures.

The rubber specimens were flat dumbbells or strips measuring from 2 to 20 cm. between gauge marks. They were stretched by dead-weight loading with manual control of the elongation, which could be observed by means of displaceable fiducial marks and a graduated scale viewed through a glass window.

The specimens, fiducial marks, and scale were contained in an enclosure through which a vigorous current of air was circulated by a blower. The air was heated by resistance coils of the type used in radiant heaters, or cooled by the use of dry ice. Consequently at the lower temperatures the specimens were surrounded by an atmosphere containing large amounts of carbon dioxide. No effects ascribable to the carbon dioxide could be noted.

#### THERMAL EXPANSION

The distance between the gauge marks on the unloaded specimens was measured over the whole range of temperatures so that all elongations could be referred to the corresponding unstretched lengths at each temperature. There was moderately good agreement between the measured lengths and those calculated by the use of the linear expansivity  $220 \times 10^{-6}$  per degree C commonly employed in this laboratory for pure-gum vulcanizates<sup>1</sup>.

Throughout the present work the percentage elongation was always measured with reference to the unstretched length at that particular temperature, and not with reference to the unstretched length at room temperature or some other fixed temperature. In other words, as the temperature was varied the distance between gauge marks was not held constant, but was kept proportional to the unstretched length at each temperature. Consequently the elongation, as just defined, was maintained constant as the temperature was varied.

The stress is defined for the purposes of the present work, in accordance with the usual practice, as the force per unit-area of original cross-section, the area being measured at room temperature.

#### RELAXATION OF STRESS

The specimens were stretched to the desired elongation and first held at a constant temperature of 25° or 70° C for about two hours, with periodic observations of the stress. On some occasions observations were extended over a period of six or eight hours.

#### STRESS-TEMPERATURE VARIATIONS

After the relaxation of stress at constant temperature, the temperature was then lowered by steps. To maintain the elongation at a constant value, it was found necessary to reduce the load. Next the temperature was usually raised while the load was again increased. In some cases the variation was repeated through a number of cycles always at constant elongation.

At the conclusion of the experiment the load was removed, and the specimen was heated to a temperature of 90–100° C in the unstressed state. It was

then stored at room temperature for about 1 or 2 days. At the conclusion of this period the distance between gauge marks was measured with a magnifying glass and a steel scale graduated in hundredths of an inch. The increase in this distance above that measured at the beginning of the experiment was expressed as a fraction of the initial distance and recorded as permanent set.

## RESULTS

## STRESS-TIME RELATIONS

The stress-time curves shown in Figure 1 are typical of those obtained at elongations of 150 per cent and less. The stress-time curves shown in Figure 2

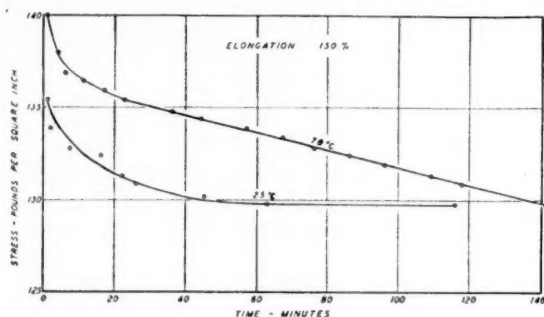


Fig. 1.—Stress-time relations for an elongation of 150 per cent at temperatures of 25° and 70° C.

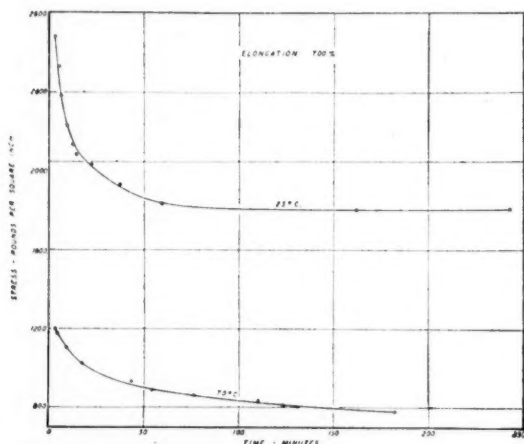


Fig. 2.—Stress-time relations for an elongation of 700 per cent at temperatures of 25° and 70° C.

are typical of those obtained at elongations of more than 500 per cent. The curves obtained at intermediate elongations show no approach to constant values of stress for times as long as six or eight hours. It is evident from Figures 1 and 2 that at 70° C the stress shows no indication of approaching a constant value after two hours, but the curve becomes approximately a straight line. Such behavior was also observed at 25° C for elongations intermediate

between 150 per cent and 500 per cent, but it is found to arise from a different cause, namely, crystallization, which will be discussed later. At 25° C outside this range of elongations, however, it is evident that the stress shows a definite approach to an equilibrium value or a quasi-equilibrium value. The exactness of approach to equilibrium at 25° C was not investigated at longer times, since the only aim was to have no appreciable further change during the one or two hours, at the most, which might be required for observations of the stress-temperature relation. This condition was satisfied with sufficient exactness, under the conditions mentioned, by a relaxation period of not more than two hours. Under the conditions where a linear decrease of stress with time was observed, on the other hand, no approach to constancy was observed at the end of six or eight hours. It was thought that if the relaxation under either set of conditions were allowed to continue for periods of the order of days, oxidation phenomena and other extraneous effects might become noticeable and mask the short time effects under investigation.

#### STRESS-STRAIN RELATIONS

The stress-strain relations obtained after a 2-hour relaxation at 25° C are shown in the upper curves of Figure 3. The same data at the lower elongations are plotted on an enlarged scale as the upper curves in Figure 4. The numerical

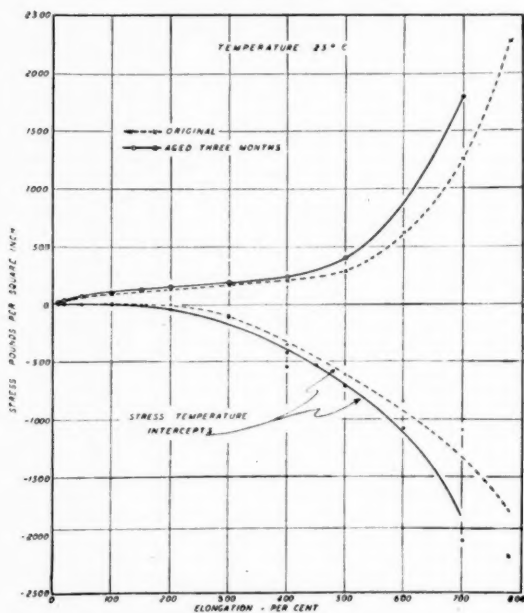


FIG. 3.—Stress-elongation relations and intercepts of stress-temperature curves at 0° K. The specimens were relaxed at constant elongation for about 2 hours at 25° C. The broken-line curves were obtained from specimens which were cured from 4 to 8 days before testing. The specimens for the solid line curve were prepared about 3 months before the tests were made.

values are given in Tables I and II. The increase in stiffness of the rubber during an aging period of three months can be noted from the two curves in each figure. It is thought probable that this increase would have been smaller

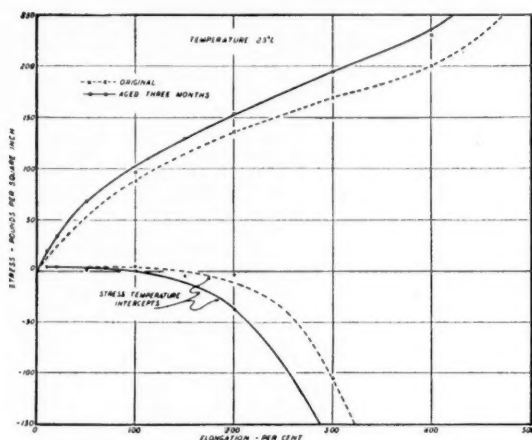


FIG. 4.—Stress-elongation relations and intercepts of stress-temperature curves at 0° K. This figure is an enlarged portion of Figure 3.

TABLE I

EXPERIMENTAL RESULTS ON STRESS-TEMPERATURE RELATIONS AFTER RELAXATION AT 25° C. SEVERAL DAYS ELAPSED BETWEEN VULCANIZATION AND TESTING

Specimen number	Elongation (per cent)	Stress at 25° C (lb. · in. <sup>-2</sup> )	Stress-temperature curve		Permanent set (per cent)
			Slope (lb. · in. <sup>-2</sup> · deg. <sup>-1</sup> )	Intercept at 0° K (lb. · in. <sup>-2</sup> )	
6	100	88.85	0.280	+5.4	0.15
5	200	136.3	0.467	-3	1.2
5	300	173.6	0.95	-109	1.2
4	400	201	1.88	-360	1.4
2	500	284	3.015	-614	2.4
1	600	624	4.6	-746	3
3	700	1257	7.85	-1093	6.3
9	780	2277	14.80	-2134	10.0

TABLE II

EXPERIMENTAL RESULTS ON STRESS-TEMPERATURE RELATIONS AFTER RELAXATION AT 25° C. THREE MONTHS ELAPSED BETWEEN VULCANIZATION AND TESTING

Specimen number	Elongation (per cent)	Stress at 25° C (lb. · in. <sup>-2</sup> )	Stress-temperature curve		Permanent set (per cent)
			Slope (lb. · in. <sup>-2</sup> · deg. <sup>-1</sup> )	Intercept at 0° K (lb. · in. <sup>-2</sup> )	
9E	10	19.6	0.0546	3.3	0.2
7E	20	34.5	0.1045	3.4	0.5
8E	50	68.0	0.223	0.7	0.2
8E	100	97.0	0.326	0.0	0.2
2C	150	130.0	0.452	-4.7	0.0
3C	200	154.0	0.646	-37.5	0.6
6B	300	195.5	0.964	-92	0.6
7B	400	230.0	2.2	-426	1.6
5G	400	231.0	2.61	-548	1.0
2G	500	402.0	3.73	-710	1.4
5D	600	661.0	5.52	-1084	1.2
4D	700	1798.0	12.9	-2048	6.7

if the rubber compound had contained an antioxidant. The values at elongations between 150 per cent and 500 per cent are affected by a continuation of crystallization after stretching, and are less reproducible than those outside this range because of variations in the completeness of crystallization.

#### STRESS-TEMPERATURE RELATIONS

Typical results of stress-temperature variations at elongations of 20 per cent, 400 per cent, and 700 per cent are plotted in Figures 5-8, respectively. Typical results over the whole range of elongations are shown in Figure 9. The numerical values of the slopes of these and a number of other stress-temperature graphs are given in Tables I-III.

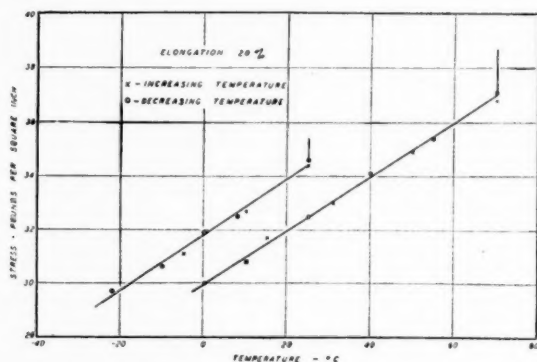


FIG. 5.—Stress-temperature relations for an elongation of 20 per cent. The vertical line at the point of highest temperature shows the amount of relaxation and the temperature at which it occurred.

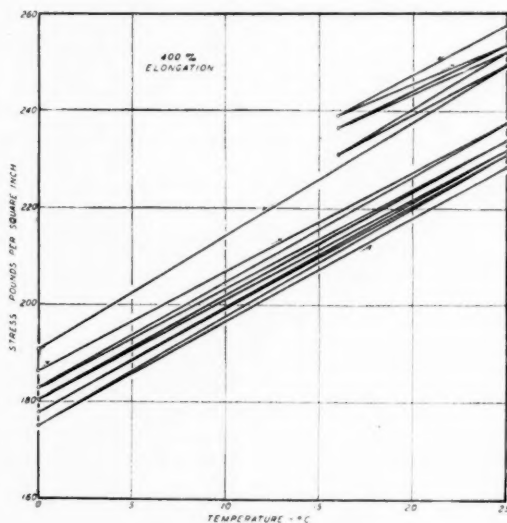


FIG. 6.—Stress-temperature relations for an elongation of 400 per cent. The specimen was allowed to relax about 2 hours at 25° C. About 2 hours more elapsed during complete cycle of events shown here.

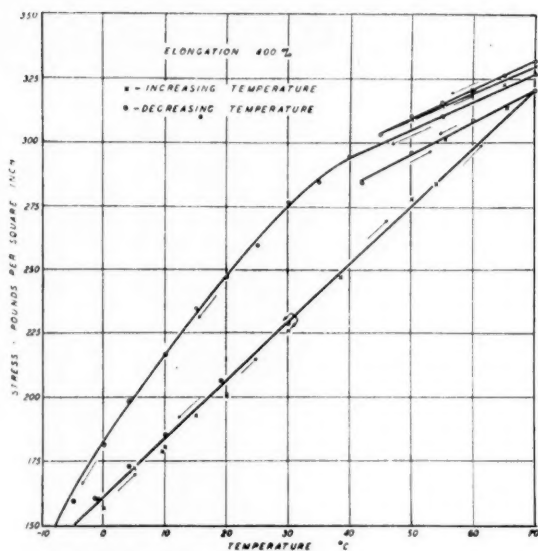


FIG. 7.—Stress-temperature relations for an elongation of 400 per cent after relaxation at 70° C.

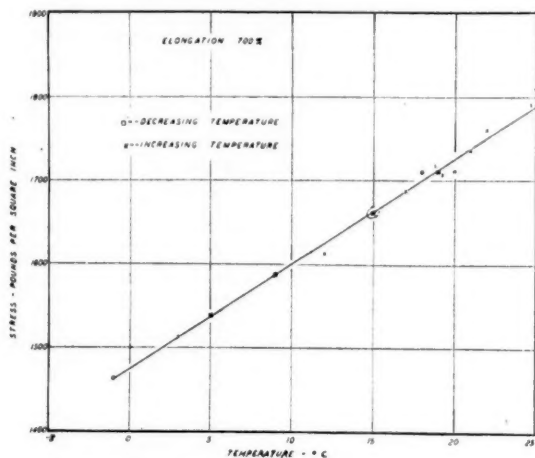


FIG. 8.—Stress-temperature relations for an elongation of 700 per cent.

#### *Relations at Low Elongations*

At elongations of 150 per cent and less, typified by Figure 5, a linear relation was always found between stress and temperature, and the same values of stress were obtained for increasing temperature as for decreasing temperature. This was approximately true even when the relaxation had been carried out at 70° C, as shown by the lower curve of Figure 5.

Repeated cycles of variation of temperature produced the same values of stress. Within the limits of observation the stress was now found to be no



TABLE III  
EXPERIMENTAL RESULTS ON STRESS-TEMPERATURE RELATIONS AFTER RELAXATION AT  
70° C. THREE MONTHS ELAPSED BETWEEN VULCANIZATION AND TESTING

Speci- men number	Elonga- tion (per cent)	Stress at 70° C (lb. · in. <sup>-2</sup> )	Stress-temperature curve		Permanent set (per cent)
			Slope (lb. · in. <sup>-2</sup> · deg. <sup>-1</sup> )	Intercept at 0° K (lb. · in. <sup>-2</sup> )	
9E	10	20.6	0.058	0.4	0.2
7E	20	37	0.101	2.4	0.5
2E	50	67.5	0.187	3.4	1.5
5E	100	100	0.277	5.0	3.0
2C	150	130	0.350	9.3	3.3
1G	200	157	0.421	13.0	7.1
4G	300	224	0.783	-45.0	8.3
1I	300	247	0.985	-82	
3F	400	321	1.34 <sup>a</sup>	-149 <sup>a</sup>	
			2.30 <sup>b</sup>	-468 <sup>b</sup>	
7G	500	382	2.93	-632	8.5
10D	600	471	3.50	-732	6.3
3D	700	783	5.41	-1072	16.0

<sup>a</sup> Amorphous.<sup>b</sup> Crystalline.

longer a function of time, but to depend solely on the elongation, the temperature, and the temperature at which relaxation had occurred.

If the temperature was raised above that at which relaxation had occurred, straight lines were not obtained, since further relaxation occurred at these higher temperatures, and the stress became again dependent on the time. After relaxation the straight lines could be obtained as before by lowering the temperature. It can be noted from Figure 5 that the value of the stress at a given temperature shows a strong dependence on the temperature at which the relaxation occurred.

The same values were obtained after relaxation at 70° C, regardless of whether or not relaxation at 25° C had occurred previously. However, the values after relaxation at 25° C were materially lowered by an immediately previous relaxation of the specimen at 70° C.

The values of the stress after a two-hour relaxation were of course found to be higher at the higher elongations, as were also the slopes of the straight lines representing the stress-temperature relation, as can be noted in Figure 9.

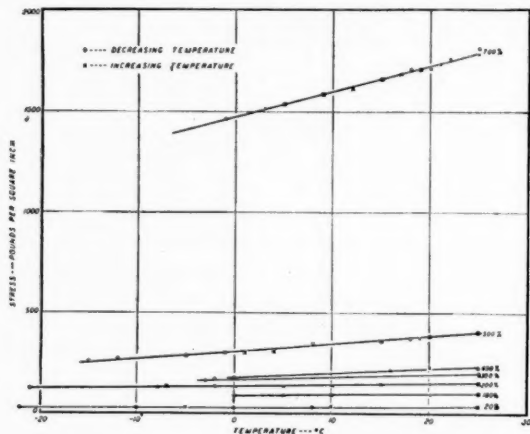


FIG. 9.—Stress-temperature relations for various elongations.

*Relations at High Elongations*

At elongations of 500 per cent and more, typified by Figure 8, the stress at any given temperature was again independent of time and was the same whether the temperature was increasing or decreasing. However, at 70° C this limit of elongation was considerably higher than 500 per cent.

*Relations at Intermediate Elongations*

At elongations intermediate between 150 per cent and 500 per cent at 25° C, the region in which the stress-time curves showed no approach to constancy, the stress-temperature relations were naturally much more complex than those outside this region. If after two hours of relaxation the temperature was lowered, the decrease of stress with time continued and often became more rapid. Consequently the stress-temperature relation was found to depend on time. If the temperature changes were made sufficiently rapidly, straight lines could be obtained similar to those in Figures 5 and 8, but the values of the stress at each temperature generally became lower as the experiment continued. A series of observations illustrating this behavior is represented by the data given in Figure 6, and refers to sample 7B listed in Table II. The slope and intercept given in this table are those of the bisector of the angle between the two lowest lines shown in Figure 6. The bisector was chosen rather than either line because it was thought that it would be less affected by the crystallization during the run. The table also lists results obtained with specimen 5G when, after a 20-hour relaxation, the temperature was lowered to -20° C. The values given are those of the slope and intercept of the line obtained as the temperature was raised from -20° to +25° C.

At the conclusion of experiments of the type just described, the permanent set previously discussed was found to be small, and this behavior appears to be the result of a continuation of crystallization after stretching rather than any effects related to flow. Crystallization will be discussed in a later section.

If the elongation is carefully selected, stress-temperature relations may be obtained showing crystallization effects which are small or negligible at the higher temperatures and quite pronounced at the lower temperatures, with subsequent melting as the temperature is raised. Thus the variations of stress resulting from the temperature variations indicated by arrows in Figure 7 illustrate the transition between the two types of behavior at a fixed elongation. In this case it can be seen that the stress at 70° C at the end of the experiment was only about 3 or 4 per cent below its original value. This may very well have been owing to a continuation of the relaxation of stress, as shown in the 70° curves of Figures 1 and 2.

## INTERCEPTS OF STRESS-TEMPERATURE GRAPHS

Stress-temperature graphs like those in Figures 5-9 may be readily extrapolated analytically to find the values of the intercepts at 0° K. There is considerable theoretical interest in the values of such intercepts, when the relations are linear, as they are here, or in general in the intercepts of the tangents to such graphs in cases in which the relation is not linear<sup>2</sup>. The actual curve representing the behavior of the rubber at temperatures below those which were observed has no bearing on this linear extrapolation, of course. The values of the intercepts found at different elongations are plotted as the lower pairs of curves in Figures 3 and 4. The numerical values are given in Tables I and II.

For a constant elongation equal to zero, it follows that the load should always be zero. The corresponding stress-temperature graph coincides with the temperature axis, and its intercept, of course, is zero. If then the intercept approaches zero at zero elongation, the positive values found at low elongations would indicate that the intercept passes through a maximum at some elongation below 50 per cent.

#### FLOW AND PERMANENT SET

When the load is removed from a stretched specimen of rubber, it does not immediately retract to its exact original dimensions. There is usually a temporary set, which disappears in a period of the order of days at normal temperatures. If the rubber is heated or swollen by solvents the temporary set disappears much more rapidly. Treloar<sup>3</sup> has shown that, even for unvulcanized rubber, the amount of permanent set which cannot be removed is a much smaller part of the total set than had been previously suspected. The permanent set is, of course, a measure of the irreversible flow which has occurred.

In the present work values found for the permanent set are given in Tables I-III. When the permanent set was more than 2 per cent of the original length, as was the case with almost all the measurements at 70° C, less reliance was placed on the results. When the permanent set was large at elongations other than those near the breaking point, the stress-time relations were like that shown for the relaxation at 70° C in Figure 1 rather than like that shown for the relaxation at 25° C. At elongations near the breaking point, the permanent set was always large. It will be noted that the compound used contained no antioxidant. If an antioxidant had been incorporated, it is probable that the flow at 70° C would have been considerably less.

#### DISCUSSION OF RESULTS

##### TEMPERATURE OF RELAXATION

A study of the results obtained when the specimens were allowed to relax at 70° C leads to the conclusion that at all elongations there is a continued decrease of stress with time. This decrease appears to be caused by flow, and is manifested by a large permanent set. For this particular compound, at least, less importance is to be attached to numerical values obtained in experiments in which relaxation was carried out at 70° C than in those relaxed at lower temperatures. The results obtained after relaxation at 25° C seem to be free from these objections, but the exact upper limit of satisfactory operation was not determined in this investigation. A dependence of the slopes and intercepts of the stress-temperature lines on the temperature at which relaxation was carried out is evident from a comparison of Tables II and III.

The previous investigators of stress-temperature relations<sup>4</sup>, studying other rubber compounds, have allowed their specimens to relax only at temperatures of about 60° or 70° C. With the exception of a single graph for an unspecified temperature<sup>5</sup>, they have not presented any evidence regarding relaxation. A recently-completed investigation<sup>6</sup> has yielded much more complete information regarding relaxation at elevated temperatures, chiefly at 100° C and above.

##### TIME OF RELAXATION

A study of the nature of the stress-time relation was not considered to be an aim of this investigation. Consequently no observations were made at very short time intervals after stretching, nor was the exactness of approach to a

constant value investigated after a long time. A different experimental arrangement would have been set up if a more detailed study of relations of the types shown in Figures 1 and 2 had been contemplated.

There is no doubt that the stress continues to decrease over periods of time much longer than those studied here. It is quite likely that such a decrease is associated with oxidation or with some other mechanism of a type not considered effective in observations extending over only a few hours.

Early studies of stress-time relations were made by Phillips<sup>7</sup> at a low elongation and by Schwartz<sup>8</sup> at an elongation of 100 per cent. A recent investigation by Mooney and coworkers<sup>9</sup> included observations over a period of eight years.

#### STRESS RELATIONS IN THE ABSENCE OF CRYSTALLIZATION

Under conditions where crystallization does not occur, namely, at elongations up to 150 per cent at 25° C in the present instance, the stress may be regarded as a quantity which depends on the elongation, temperature, time, and previous thermal and mechanical history of the specimen. A brief summary of the phenomena yielding the experimental results described in the preceding sections will serve to make the nature of the dependence clearer. The upper limit of temperature is taken as 25° C and the lower limit as about -20° C. The times considered will be of the order of hours rather than days, so effects of oxidation need not be considered. The theoretical basis of the phenomena is not considered in the present work.

At temperature  $T$  and elongation  $E$  there is a corresponding stress value  $S_E$  representing an equilibrium. The actual value  $S$  of the stress at a given time may not equal the equilibrium value  $S_E$  because of the lapse of insufficient time following some change in elongation or temperature. However, there is a closer and closer approach to  $S_E$  as time goes on. At 25° C the stress in the pure-gum vulcanizate studied attains a value within a few per cent of  $S_E$  in one or two hours after first application of a load. Thereafter there are no further changes with time, provided the elongation is unaltered and provided the temperature is not raised above that at which the relaxation occurred. No time effects are introduced by lowering the temperature and then raising it to the relaxation temperature or by repeating the variation a number of times. The stress-temperature relation under these conditions is linear.

A previous heating of the unstretched rubber which does not lead to oxidation appears to have no influence, but the stress is found to be temporarily less than  $S_E$  if the specimen has been heated to a temperature higher than  $T$  while stretched, or if it has been stretched to an elongation greater than  $E$ . Since time is required for the approach to  $S_E$ , it is clear that immediately after any stretching for the first time  $S$  is greater than  $S_E$ . Immediately after any amount of retraction from a condition in which  $S$  has approached an equilibrium value,  $S$  is less than  $S_E$ . The increase of  $S$  with time following a reduction of elongation and its approach to  $S_E$  from lower values was observed by Meyer and Ferri<sup>5</sup>, and has been confirmed by direct experiment in our laboratories. If the load is completely removed  $S$  is reduced to zero, which is less than the value of the  $S_E$  corresponding to the residual elongation. In time the residual elongation or temporary set disappears almost completely and the corresponding value of  $S_E$  approaches zero.

#### CRYSTALLIZATION

The crystallization of rubber on stretching has often been mentioned as a factor of importance in determining its elastic behavior. Nevertheless, most

previous writers have been unwilling or unable to make the definite correlations which are desirable in this connection.

Three distinct regions in the stress-strain curve of rubber were recognized as early as 1910, when Schwartz<sup>8</sup> named them stage 1, stage 2, and stage 3. Wiegand and Snyder<sup>10</sup> discussed the regions in considerable detail under the designations region *A*, region *B*, and region *C*. A similar division was made by Williams and Sturgis<sup>11</sup> a few years later. Wiegand and Snyder were rather cautious about ascribing the effects to definite crystallization and preferred to speak merely of "profound structural changes". The other writers made no attempt whatever to explain the effects observed.

These regions appear well defined in the results of the present work. In region *A*, which extends up to an elongation of about 150 per cent in the present compound at 25° C, we may say that there is no crystallization on stretching, or at any other time during the experiment. In region *B*, which includes elongations from about 150 to 500 per cent, the crystallization which occurs on stretching is partial, and additional crystallization continues for a considerable time. In region *C*, at elongations greater than 500 per cent, the crystallization which occurs on stretching and possibly during relaxation is so nearly complete that no further crystallization could be observed during the entire period of observation. A lowering of the temperature does not lead to any additional crystallization, nor does a return to the temperature at which the rubber was stretched give rise to melting.

Relaxation and the other stress relations discussed in the preceding section as characteristic of region *A* are also present in region *B* with a superposition upon them of the additional complexities associated with continuing crystallization. The simpler stress relations are again evident in region *C*.

The decrease of stress with continuing crystallization in region *B* has been noted previously<sup>5</sup>. In fact, working with unvulcanized rubber at -25° and 0° C, Smith and Saylor<sup>12</sup> found that crystallization can continue to such an extent that the stress not only decreases to zero but even becomes negative. If the distance between the ends of the specimen is held fixed, the specimen becomes bowed at the center. This effect was found to be small or negligible in region *C*.

Crystallization in stretched rubber has been investigated by previous workers using x-rays<sup>13</sup>, volume changes<sup>14</sup>, and double refraction<sup>15</sup>. It appears from the present work that stress-time or stress-temperature relations may also be used to locate the regions of elongation and temperature in which crystallization occurs and to gain additional information about its nature.

#### APPLICATION OF THERMODYNAMICS TO STRESS-TEMPERATURE DATA

The results of studies of this kind may be used to evaluate the entropy and energy terms appearing in equations describing the elastic behavior of rubber. In fact, most of the previous observers<sup>16</sup> in this field have applied thermodynamic equations of the types discussed by Gerke<sup>17</sup> to their experimental data. The scope of the present paper does not permit such an application, with the necessary qualifications. This paper aims, rather, to describe and present at least some of the necessary experimental results.

It might be pointed out once again that the experiments described in the present paper were carried out at constant elongation. In this manner the data did not require the corrections for thermal expansivity applied by previous observers<sup>18</sup> who observed stress-temperature relations at constant length and



calculated from them stress-temperature relations at constant elongation. However, since the present work was initiated, theoretical interest, as exemplified in the work of James and Guth<sup>19</sup>, seems to be more concerned with stress-temperature relations at constant length than was previously the case. Relatively simple relations can be derived by which the stress-temperature relations at constant length can be obtained from the results presented here. The intercept of each stress-temperature relation at constant length is greater than that at constant elongation, while the slope is less. An experimental study of these relations is in progress.

### SUMMARY

Stress-temperature relations at constant elongation have been investigated for a pure-gum vulcanizate of natural rubber. The rubber was first allowed to relax for about two hours at constant elongation and constant temperature to minimize the effects of short time relaxation of stress. The stress, except under special conditions, was changing very little at the end of this time. The stress-temperature relations for temperatures below the relaxation temperature could be represented by straight lines. The values of the slopes and intercepts of these lines are presented in tabular form. The stresses at the end of the relaxations were used as the basis of stress-strain curves. Crystallization was found to be an easily-recognized factor of considerable importance in the interpretation of the results.

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## SPEED OF RETRACTION OF RUBBER\*

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### INTRODUCTION

The most characteristic property of rubberlike materials which distinguishes them from other substances is the speedy and forceful retraction which occurs when they are released after stretching. Compounders use the "snappy" feel of stocks to judge quality and cure. Practically nothing has been known about the actual velocities of rubber retractions, which undoubtedly are related to the molecular structure, modulus, internal friction, temperature, and other variables. The problem of determining state of cure has been accentuated by the introduction of various types of synthetic rubber and vulcanizing systems so that there is a need for new means of evaluating state of cure.

A brief description of the electronic method used for measuring the velocity of free retraction of rubber has been published<sup>1</sup>. High-speed photographs showing the wave front of the retracting rubber band were included. Mrowca, Dart, and Guth<sup>2</sup> have described a method of measuring the retraction velocity by a smoked drum and a stylus attached to the rubber strip. They also have published similar photographs.

A few experiments are described in the literature, the object of which was to correlate the modulus with the velocity of an impulse along a rubber strip. These papers are discussed by Whitby<sup>3</sup>, and show that the speed of retraction was measured as early as 1872.

The velocity acquired by a retracting strip of rubber is quite high—of the order of 100 miles per hour or more—so it has been difficult to measure or photograph the "snap" which takes place in a few thousandths of a second. The method described below permits such measurements to be made with facility, and may give information of much value from both a theoretical and practical standpoint.

### METHOD

A schematic diagram of the apparatus used for measuring speeds of retraction is given in Figure 1. The rubber strip ( $16.5 \times 1.9 \times 0.2$  cm.) is held in a horizontal frame having one grip (No. 1) fixed and one (No. 2) which slides in a channel in the frame. A wire cable which may be wound up on a spool is fastened to the movable grip so that, by turning a crank, the test-strip may be extended to any desired elongation, and held there by a ratchet. The grips are of the familiar eccentric roller type adapted for quick release.

The strip intercepts two narrow beams of light from the lamps, which are directed at photocells A and B. The beams are 2.65 cm. apart at the rubber strip. When the strip is released from grip No. 1, it retracts and permits light to fall on photocell A. The photocell current puts a negative charge on the grid of the 9001 tube so that its plate current is cut off. When this occurs, the

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grid of the 6J5GT tube becomes positive, and the tube conducts a current which is limited by the cathode resistor. This current flows into the capacitor in the plate circuit of the 6J5 tube, so that it begins to acquire a charge. When the rubber strip has retracted sufficiently for light to fall on photocell *B*, however, the photoelectric current produced causes the 9001 tube to become conducting again, which biases the 6J5 beyond plate current cut-off. The capacitor retains the charge it had accumulated, which depends on the time the charging current was flowing. The voltage on it is measured by a vacuum-tube voltmeter, which consists of an ordinary bridge circuit using a 6C8G twin triode and a microammeter. The voltmeter has two ranges, 0 to 5 volts and 0 to 15 volts. A conventional regulated power pack supplies the power. Electronic timing circuits of this general nature have been used previously for a variety of purposes<sup>4</sup>.

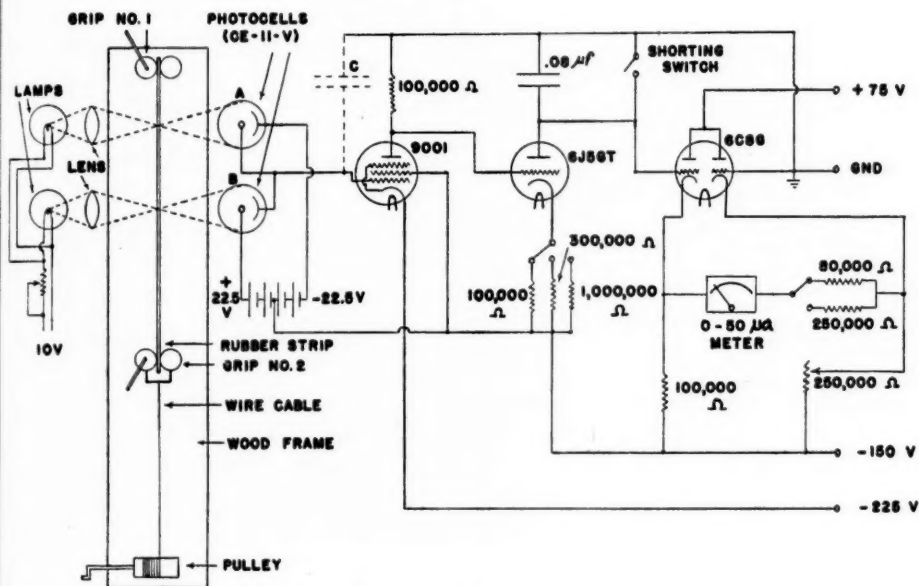


FIG. 1.—Schematic diagram of apparatus.

Since a much higher charging voltage is used (150 volts) than is ever acquired by the condenser (15 volts), the voltage measured was found to be practically proportional to the time interval. Calibration of the circuit was carried out by measuring accurately the condenser capacity and the charging current. The voltage is the integral of the current with respect to time divided by capacity. The speed of the rubber strip equals the distance between the light beams, divided by the time. Figure 2 is a photograph of the apparatus.

The design of the optical system and the photocell circuit is critical because of the short time intervals to be measured. The input capacity for the 9001 tube, plus the capacity of the photocells and wiring, must be as small as possible. This capacity is represented by the dotted condenser *C* in Figure 1. When the light impinges on photocell *A*, the current charges this capacity to about 22 volts negative. The current of photocell *B* then discharges the capacity and

brings the voltage on the 9001 grid back to its original value. Thus it is obvious that if photocell *A* is not properly illuminated, it will take too long to start the charging action for the main 0.08- $\mu$ f condenser, so the time measured will be shorter than the actual interval. Similarly, if the current from photocell *B* is too low, the charging current is not cut off soon enough and the velocity will appear lower than it really is.

To minimize these effects, the wiring and arrangement of parts in the housing were such that the capacity *C* amounted to only 9.5  $\mu$ f. The photocells each required about  $\frac{1}{2}$  lumen of light flux to give the desired currents. To provide sufficient light, high-aperture lenses were used in the illuminating system. The light sources were ordinary radio pilot bulbs, selected for the straightness of the filaments. The images of these filaments were projected on the rubber strip by 12.8-mm. focal length lenses (10-mm. diameter) which magnified the images about 3 times.

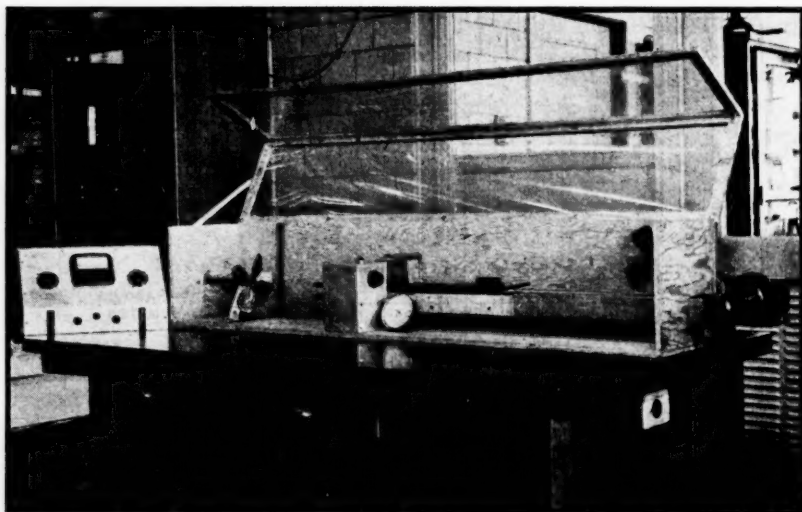


FIG. 2.—Photograph of apparatus.

The photocells were placed far enough behind the images so that the flux spread out to cover most of the cathode surfaces. A microammeter in series with the photocells permitted the lamp brightness to be adjusted to the working range in case of bulb blackening, or replacement with a new lamp. The effect of photocell current on the accuracy of measurement is shown in Figure 3. If the current is too small, the trigger action is so slow that it becomes an appreciable part of the time interval being measured, and thus the measurement gives too high a velocity. By maintaining the photocell current at a value of about 5 microamperes, the trouble was avoided for all velocities encountered.

A check on the calibration of the device was made by dropping a steel ball past the photocells. A wide tail was fastened to the ball to intercept the light beams. The ball was dropped from a height of 348 cm. so that it had acquired a velocity of 827 cm. per second when the measurement was made. The measured value was  $828 \pm 10$  cm. per second.

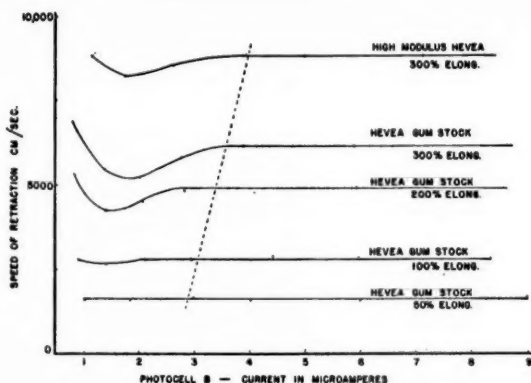


FIG. 3.—Effect of photocell current on measurements.

The precision of the apparatus (that is, the consistency and reproducibility) is good, for there is very little scattering of points on the plots of the data, and measurements can be repeated to within about 5 per cent.

The consistency of the readings was further checked by placing a set of four small mirrors in the path of one of the light beams in such a way as to displace the beam parallel to itself. In this way the distance between the beams at the point at which they were intercepted by the test-strip was varied from 1 to 5 cm. Using the same rubber strip at the same elongation, several different time intervals were measured for one velocity. This method extended the calibration to time intervals as low as 150 microseconds, which corresponds to a velocity of over 15,000 cm. per second. A typical calibration curve is shown in Figure 4.

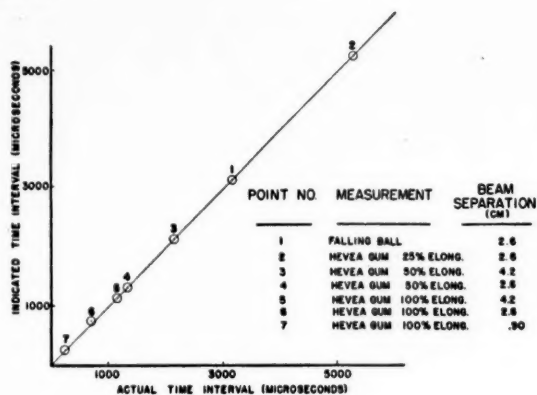


FIG. 4.—Calibration curve.

Probably the greatest source of variability is the permanent set and stress relaxation of the stocks, both of which would tend to reduce the velocity. To minimize these effects, the measurements were always made at low elongations first proceeding to successively higher elongations. The length of the strip held in grip No. 1 was kept the same by always lining up the end of the strip with a mark on the grip. Grip No. 2 was reset after each measurement to correct for any slippage and permanent or temporary stretch.

If the rubber strip is released immediately after stretching to the desired elongation, stress relaxation is a minimum and the highest velocity is observed. If the strip is held in a stretched position for several seconds, an equilibrium condition is reached so that a lower velocity is obtained which is practically independent of the time before release. This is true only for stocks with low plastic flow. Butyl stocks, or even Hevea stocks which are undercured or very cold, will take longer to reach an equilibrium condition. However, for the purposes of comparison, a time interval of 30 seconds was consistently allowed for the strip to come to equilibrium.

For the sake of simplicity, all measurements were made when the moving end of the strip was 2 inches from grip No. 1. This corresponds to about 50 per cent of full retraction at 100 per cent original elongation, or 25 per cent retraction in the case of 200 per cent original elongation. A more refined system might include a mechanical linking of the phototube housing to the crank which extends the rubber strip so that the housing would be moved further from grip No. 1 at higher elongations, and all measurements would be made at the same per cent of full retraction. However, it was not felt that the additional complications of such a system were worthwhile.

#### NATURE OF THE RETRACTION

A stretched strip of rubber which is suddenly released does not retract as a whole, as a weighted spring would do. Instead the retraction occurs at the free end first and travels in a wave along the strip. In an ideal case, the wave would be reflected from the fixed end, so the strip would stretch out again. Actually, however, the energy of the retraction is dissipated by the inelastic impact at the grip and by the flopping of the retracted strip. Longitudinal wave transmission in bars has been analyzed from an engineering standpoint by Donnell<sup>5</sup>.

It might be anticipated that the velocity of the retraction wave would be essentially constant if the band is of uniform cross-section. Measurements of the velocity at different states of retraction (made by positioning the light and photocell assembly at different points along the strip) show that the velocity actually increases slightly as the retraction progresses. This is illustrated in Figure 5. A probable explanation for this is that the small "dead" mass held in grip No. 1 retards the retraction at first.

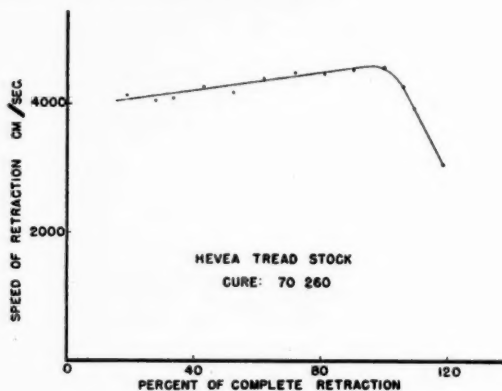


Fig. 5.—Speed acquired during retraction.

The retraction wave can be shown very plainly by means of photographs taken with a high-speed stroboscopic light of the Edgerton type. Some typical photographs are shown in Figures 6a and 6b. The first picture is a balloon in

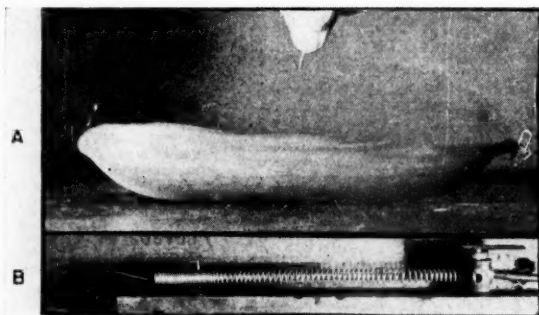


FIG. 6A.—High-speed photographs of rubber in retraction. A, balloon bursting. B, steel spring, about 35 per cent retracted.

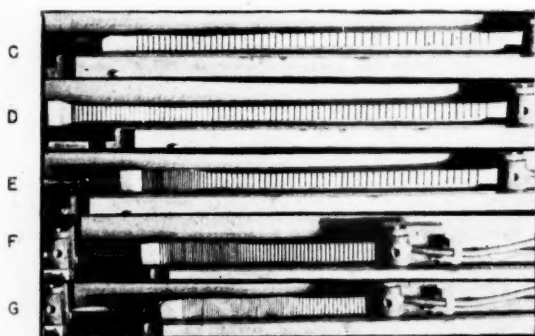


FIG. 6B.—C, Butyl gum stock, about 30 per cent retracted. D, Hevea gum stock, about 5 per cent retracted. E, Hevea gum stock, about 40 per cent retracted. F, Hevea gum stock, about 55 per cent retracted. G, Hevea gum stock, about 70 per cent retracted.

the act of bursting. A faint outline of the original shape can be seen. The retraction wave has advanced about halfway down the sides of the balloon, so that the lower half of the balloon is as yet unaware that it has been pricked by the pin. A retracting steel spring is shown for comparison with rubber. In Figure 6B, the very broad wave front of Butyl gum stock is seen in contrast to the sharp front for Hevea gum stock in four stages of retraction.

The local elongation along some of the retracting strips, obtained by measuring the distances between the ruled lines on the photographs, has been plotted in Figure 7. This plot shows more clearly the sharp wave front of the Hevea gum and the steel spring. Butyl rubber, on the other hand, having a high internal friction and low resilience, has a broad wave front which amounts simply to a gradual reduction in elongation along the entire length of the strip.

The form of the retraction is predicted by the classical theory of a vibrating bar<sup>6</sup>. The familiar wave equation which applies is:

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2} \quad (1)$$

Here  $u$  is the displacement and  $v[(E/\rho)^{1/2}]$  is the retraction wave velocity.  $E$  is Young's modulus and  $\rho$  is the density.

To simplify the boundary conditions, the case of a stretched rubber strip, the two ends of which are released simultaneously, was considered. Since the center of the strip remains at rest, the description of the retraction of one-half of the strip applies to our experiments.

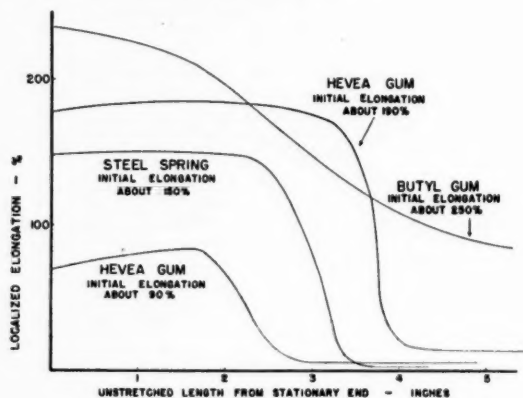


FIG. 7.—Local elongation vs. unstretched length.

The boundary conditions are:

$$\begin{aligned} u &= 0 \text{ at } x = L/2 \\ \partial u / \partial x &= 0 \text{ at } x = 0 \text{ or } L \\ \partial u / \partial t &= 0 \text{ at } t = 0 \\ u &= (-\epsilon L/2) + \epsilon x \text{ at } t = 0 \end{aligned}$$

The solution was found to be:

$$u = \sum_{n=1,3,5,\dots}^{\infty} \frac{4\epsilon L}{n^2\pi^2} \cos \frac{n\pi x}{L} \cos \omega_n t \quad (2)$$

$L$  is the length of the strip,  $\epsilon$  or  $(\partial u / \partial x)_{t=0}$  is the unit elongation, and  $\omega_n = n\pi v / L$ .

The following numerical values were used as typical for Hevea gum stock:  $E = 9.6$  kg. per sq. cm.,  $\rho = 0.92$  g. per cc.,  $L = 25.4$  cm.,  $\epsilon = 3$  (300 per cent elongation). Good convergence was obtained by using five terms of the series.

To compare the shapes of the calculated wave fronts with those observed experimentally, it was necessary to differentiate  $u$  with respect to  $x$  for fixed values of  $t$ . This gives the local elongation as a function of the distance from one end. The sharp wave fronts calculated for three values of the time are shown in Figure 8, and are similar to those observed for Hevea gum stock and plotted in Figure 7.

If a viscous friction term,  $2k(\partial u / \partial t)$ , is included in the left-hand side of Equation (1), the solution is, for the same boundary conditions as before:

$$u = \sum_{n=1,3,5,\dots}^{\infty} \frac{4\epsilon L}{n^2\pi^2} e^{-kt} \cos \frac{n\pi x}{L} \frac{\cos(\omega_n t - \phi_n)}{\cos \phi_n} \quad (3)$$

Here

$$\phi_n = \tan^{-1} \left( \frac{k}{\omega_n} \right), \quad \text{and} \quad \omega_n = \left[ \left( \frac{n\pi v}{L} \right)^2 - k^2 \right]^{\frac{1}{2}}$$

Using the same numerical values as before and  $k = 300 \text{ sec.}^{-1}$ , the plots for  $\partial u / \partial x$  for  $t$  equal to 2 and 3 milliseconds are given in Figure 8. They show a broadening of the wave front compared to the case calculated without friction. From comparison of the calculated and observed wave fronts, it appears that the value selected for the friction was considerably less than the actual friction for Butyl gum stock and somewhat larger than that for Hevea gum stock.

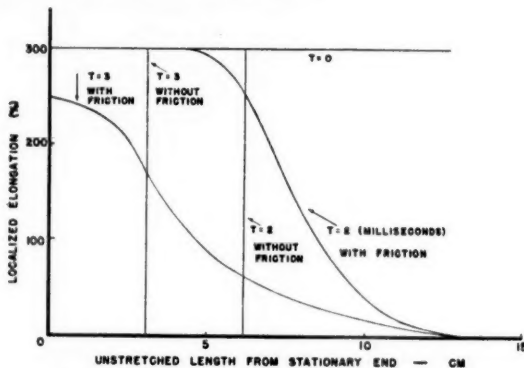


FIG. 8.—Theoretical curves with and without friction.

The velocity actually measured is not that of the wave front, for which  $v = (E/\rho)^{\frac{1}{2}}$  but is that of the end of the strip. The relationship between the two may be obtained to a first approximation by assuming that the potential energy of the stretched strip is all converted into kinetic energy. For a strip of unit cross-sectional area:

$$\text{P.E.} = E\epsilon \frac{1}{l} \int_0^l \epsilon x dx$$

where  $E$  is the elongation and  $l$  the unstretched length.

$$\text{K.E.} = \frac{1}{2} m v_m^2 = \frac{l\rho}{2} v_m^2$$

where  $v_m$  is the measured velocity.

Equating these quantities gives:

$$v_m = \epsilon(E/\rho)^{\frac{1}{2}} = \epsilon v$$

Assuming a constant modulus (Hooke's law) and density per unit length based on unstretched dimension, the velocity  $v_m$  should be directly proportional to the elongation and to the square root of the modulus divided by the density. These are reasonable assumptions because the modulus of a good gum stock, such as Hevea, is nearly constant up to several hundred per cent elongation. However, there are several other factors which are not considered by this simple relationship. The internal friction reduces the velocity somewhat. The mass of that part of the strip held by grip No. 1 provides additional inertia which reduces the velocity measured. Plastic flow and the sidewise motion of the elements of the strip in expanding to the unstretched width



would have a similar effect. The velocity would also be reduced by the reduction of modulus caused by the Joule cooling of the strip owing to adiabatic contraction. For Hevea gum stock, the measured velocities are actually somewhat higher than those calculated from stress-strain data. This is probably associated with the fact that the modulus of rubber increases with the testing speed.

#### COMPOSITION OF STOCKS

To compare the effect of carbon black loading in stocks, a series of natural rubber and GR-S stocks was compounded as shown in Table I.

TABLE I  
PARTS BY WEIGHT

Compound	A	B	C	D	E	F	G	H
Smoked sheet	100.0	100.0	100.0	100.0				
GR-S					100.0	100.0	100.0	100.0
Mercaptobenzothiazole	1.35	1.35	1.35	1.35	1.5	1.5	1.5	1.5
Stearic acid	3.0	3.0	3.0	3.0	2.0	2.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Softener	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sulfur	2.75	2.75	2.75	2.75	2.0	2.0	2.0	2.0
Channel black (E.P.C.)	50.27	40.22	30.16	20.11	59.00	49.20	39.40	19.70

The compositions of the gum stocks tested are given in Table II.

TABLE II  
PARTS BY WEIGHT

Compound	N	O	P	Q
Smoked sheet (Hevea)	100.0	100.0		
GR-I (Butyl)			101.5	
GR-M (Neoprene)				100.0
Mercaptobenzothiazole	.5		.5	
Tetramethylthiuram disulfide			1.0	
Piperidinumpentamethylene dithiocarbamate		2.0		
Stearic acid	1.0			.5
Zinc oxide	5.0	2.0	5.0	5.0
Magnesium oxide				4.0
Phenyl $\alpha$ -naphthylamine				2.0
Sulfur	3.0	2.0	2.0	

To note the effect of mixing GR-S and Hevea, a series of stocks was compounded with a good GR-S tread stock as a base, with different percentages of Hevea added. The acceleration of the stocks was adjusted to give the same rate of cure. Thus the 100 per cent Hevea stock is not a typical tread stock, and this fact should be considered when comparing its properties with the other stocks. The compositions are given in Table III.

TABLE III  
PARTS BY WEIGHT

Compound	I	J	K	L	M
GR-S	100	75	50	25	
Smoked sheet		25	50	75	100
Benzothiazyl-2-monocyclohexyl sulfenamide	1.6	1.3	1.0	.75	.5
Stearic acid	1.6	1.3	1.0	1.0	1.0
Zinc oxide	3.0	3.0	3.0	3.0	3.0
Softener	4.0	4.0	4.0	4.0	4.0
Sulfur	1.6	2.0	2.3	2.65	3.0
Channel black (E.P.C.)	45	45	45	45	45

The stocks of Tables I and II were formulated by J. H. Fielding and those of Table III by E. Cousins.

### DISCUSSION OF MEASUREMENTS

The velocity of the retraction of a rubber strip obviously depends on the density and modulus of the stock. Other important factors are the internal friction, plastic flow, and stress relaxation of the material before it is released. These effects are illustrated by plots of data obtained under various conditions.

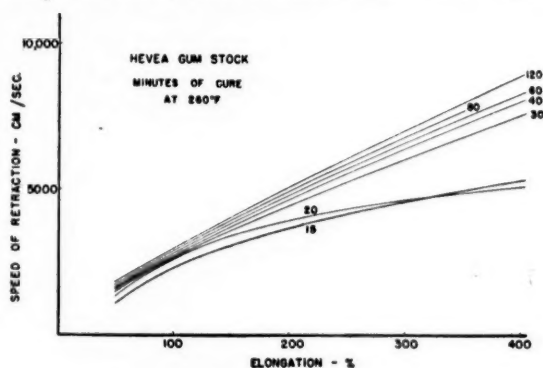


Fig. 9.—Speed of retraction *vs.* elongation.

Figure 9 shows the rise in speed of retraction with elongation. These curves are almost straight lines, quite different from the ordinary stress-strain curves, showing that other factors beside the modulus affect the speed of retraction. There is a definite change in slope of all the curves between 0 and 100 per cent elongation which may be related to the shape of the stress-strain curve. The continued curvature of the two uncured samples is undoubtedly due to the high plastic flow of these stocks.

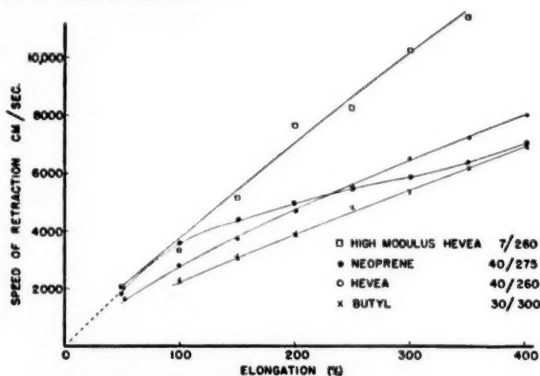


Fig. 10.—Speed of retraction of gum stocks *vs.* elongation.

Figure 10 shows how Hevea rubber compares with synthetic polymers. The Neoprene stock gives a comparatively high velocity at low elongations, but the higher internal friction of this stock and of the Butyl stock results in lower velocities at high elongation.

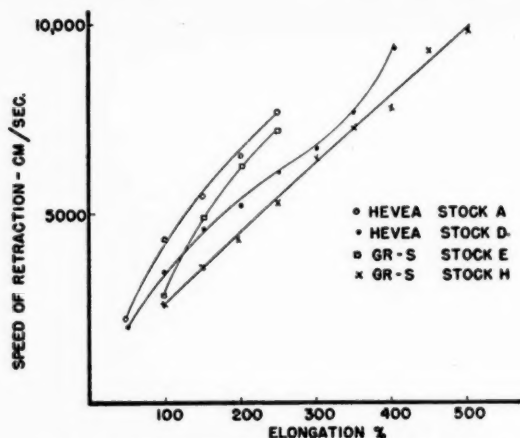


Fig. 11.—Speed of retraction of tread stocks vs. elongation.

Figure 11 shows the effect of elongation on the speed of retraction of loaded stocks. These curves are very nearly straight lines. The high forces required to give the elongations above 300 per cent may have resulted in slippage at the grips, so there is some scattering of the points. Until a better means of clamping the test-strips has been devised, no attempt to interpret such small deviations will be made.

One of the most dependable criteria for state of cure, even though not scientific, is the "snappy" feel of the stock. Few quantitative tests are available which give a definite means of determining the best cure for general purposes if the stock is not compounded for a specific property, such as tensile strength. One of the important results of curing a stock is the reduction of plastic flow and increase in modulus. Since the speed of retraction is affected so greatly by these properties, it seems likely that it should show the difference between a properly cured and undercured stock.

Figures 12 and 13 are plots of speeds of retraction for various cures for typical stocks. Although the Neoprene gum stock does not show a large effect,

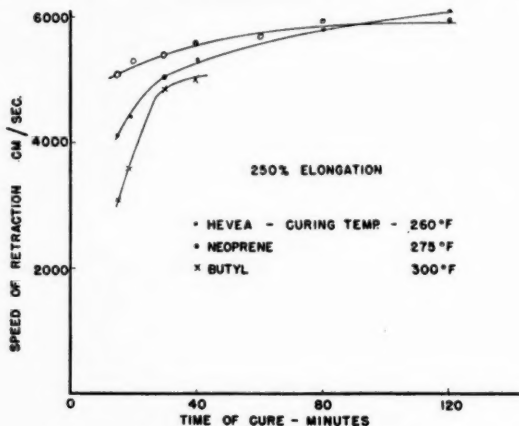


Fig. 12.—Speed of retraction of gum stocks vs. cure.

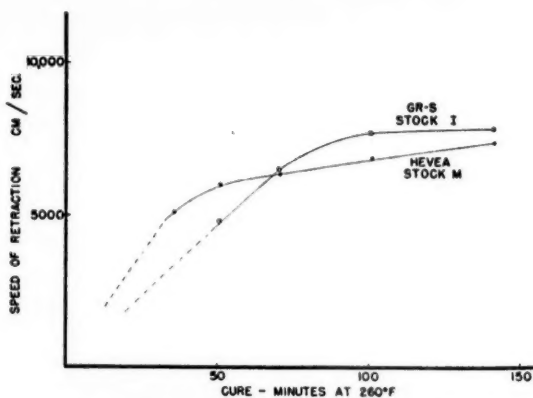


Fig. 13.—Speed of retraction of tread stocks vs. cure, 250 per cent elongation.

there is a more or less sharp bend in each of the curves for the other stocks. The bend is a result of the reduction in plasticity of the stocks as the cure proceeds, which is accompanied by increasing modulus and decreasing internal friction. In every case it appears at approximately the curing time denoted by the compounders as the "best" cure. The position of this bend in the plots is not greatly affected if the 30 seconds allowed for the strip to come to equilibrium before releasing from the grips is increased to two minutes. However, the angle of the bend is increased so that the point of "best" cure is less definite.

To determine the effect of temperature on the speed of retraction, the apparatus was placed in an enclosure so that the temperature of the air surrounding the test-piece could be controlled. The strips were conditioned at the desired temperature before stretching. Figure 14 shows the effect of

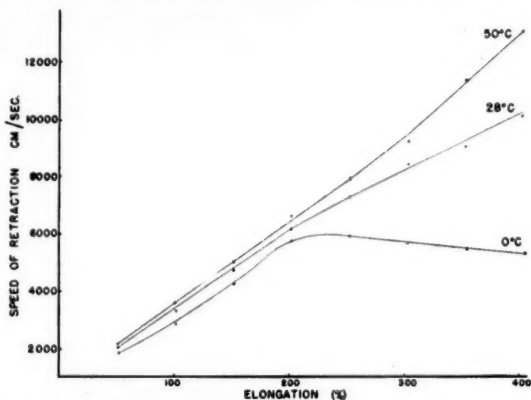


Fig. 14.—Speed of retraction vs. elongation at different temperatures.

temperature on the speed of retraction for a Hevea gum stock. The reduction in speed at low temperatures for this stock might be explained as caused by an increased permanent set and internal friction of the stock and an increased crystallization. At higher temperatures, increased retractive force increases the speed of retraction. The reduction in velocity of the Hevea gum stock

beyond 200 per cent elongation at 0° C is evidently due to the formation of crystallites. Several checks were made to make certain of this unexpected behavior.

Figure 15 illustrates the effect of loading with carbon black. The speed of retraction rises almost linearly with loading, although much less rapidly than

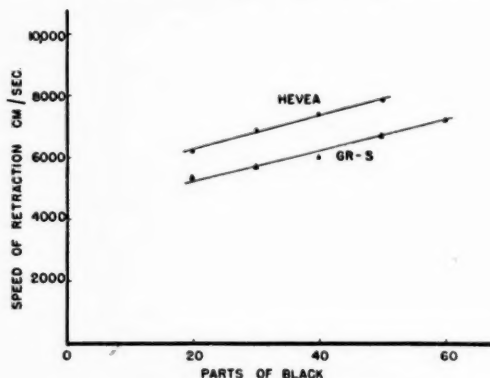


FIG. 15.—Speed of retraction vs. loading.

the modulus does, due to the fact that the internal friction also increases. Differences in internal friction rather than modulus are responsible for the lower velocities of GR-S compared to Hevea in this plot. The data for Figure 15 were secured for the stocks of Table I at 250 per cent elongation and best cure.

Figure 16 shows how various properties of a GR-S tread stock are affected by substituting increasing percentages of natural rubber for the synthetic

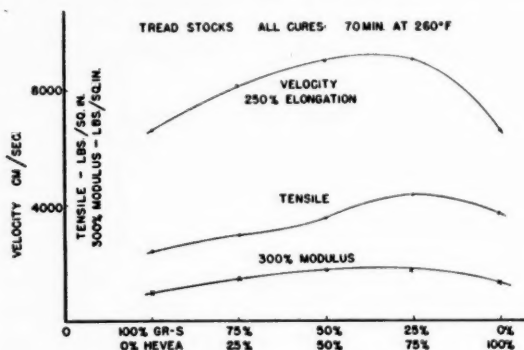


FIG. 16.—Effect of adding Hevea in a GR-S compound.

polymer. As stated before, the 100 per cent Hevea rubber stock is not typical of a natural rubber tread stock, but is the result of the consistent compounding used in the series. The apparently inferior properties are not to be encountered in normal practice. The main purpose of this chart is to show how the speed of retraction varies with other standard properties. It may be observed in general that the speed of retraction test appears to be more sensitive than the other

tests under selected conditions. Its ultimate value will probably depend on the results of more critical experiments in the fields where this survey indicates that it may have some usefulness. Under proper circumstances, there is a possibility that it could become a useful criterion for quality and cure.

### CONCLUSIONS

The results obtained with this apparatus show that interesting information can be obtained by making measurements of the speed of retraction under various conditions and by comparing different compounds and polymers. This information should be of value both for a better understanding of the molecular structure and the forces involved and also as a practical means for properly qualifying the material as to its elastic properties.

The device appears to have an immediate practical application as an aid to the compounder in determining the "best" cure.

The apparatus is quite simple to use and if properly designed is sturdy and dependable. Reliable measurements could be made at the rate of about fifty per hour without requiring much skill. Thus, the speed of retraction measurement would be practical for a routine, standard test.

### ACKNOWLEDGMENT

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# THE STIFFNESS OF RUBBER ON BENDING, OR ITS DYNAMIC HARDNESS \*

## THE METHOD OF RESONANCE VIBRATIONS

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When used for industrial purposes, vulcanized rubber products must often meet an extraordinarily complex set of requirements. Not only are they subjected to shearing stresses, but they must withstand various compression, tensile and bending stresses, such as are encountered in V-belts, conveyor belts, and diaphragms. In many cases these stresses are very rapid, and consequently a knowledge of the dynamic stiffness of a product may often be of technical interest and value. As will be shown, this dynamic stiffness cannot be estimated directly in terms of static hardness, for it depends also on the character of the fillers or pigments in the rubber.

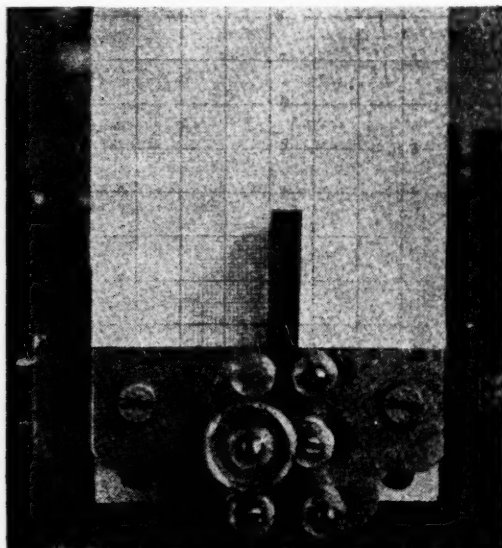


FIG. 1

It has been found that the bending stiffness of vulcanized rubber can be determined in a simple and precise way by fixing rigidly a prismatic test-specimen at one end, and setting up bending vibrations in the test-specimen by

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 20, pages 3-5, January-February 1944.

vibrating the attachment which holds it. By changing the length of the test-specimen, a sharply defined point of resonance is found. From the resonance length  $l_r$ , the cross-sectional area and the density, it is possible to calculate the effective modulus of elasticity  $E_B$  for the particular frequency of bending vibration.

In the case to be described, the frequency of an industrial alternating current, *viz.*, 3000 oscillations per minute (50 Hertz units), was used to induce vibrations in the rubber under investigation. Figure 1 is a photographic reproduction of the apparatus. A resonance oscillator carries the attachment for holding the prismatic test-specimen. The amplitude of the oscillator is measured triangularly by the well known method. The activating mechanism is electromagnetic, but obviously it is possible also to use a mechanical activator, based on the eccentric principle. Figure 2 shows the apparatus in operation during a test.

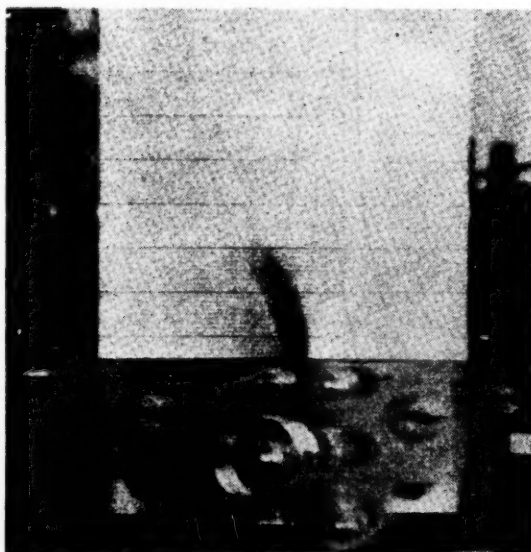


FIG. 2

With test-specimens of soft vulcanized rubber, 5–20 mm. thick (measured in the direction of vibration), the resonance length is 15–80 mm. at 50 Hertz units frequency. The width of the test-specimen has no influence on the results. The sharpness of the resonance is evident in the curves shown in Figure 3. In the case of heavily loaded rubber mixtures with low rebound-resilience, the resonance point is naturally less sharp.

Nevertheless it is possible to make an exact determination of the resonance length in convenient fashion by the use of stroboscopic illumination, with alternating light of the same frequency as the vibration, and with adjustable phase. The phase is so adjusted that the source of light (glow lamp) illuminates one of the reversal points of the vibrator. Under these conditions, the prismatic test-specimen appears to lie exactly perpendicular to the resonance, while it appears to be bent below the resonance to the right and above the

resonance to the left, or *vice versa*. This method was used to measure all types of vulcanized rubber up to hard rubber.

To compare this new method with conventional static testing methods, systematic measurements of several series of vulcanizates were made. Table 1 shows the data obtained with a bending frequency of 50 Hertz units. In this table  $E_Z$  is the stress in kg. per sq. cm. (based on the original cross-section) at 100 per cent elongation, and  $E_D$  is the compression modulus in kg. per sq. cm., determined between flat platens after the load had been applied for 10 seconds on a test-specimen 6 mm. high and of 2 sq. cm. face area. The cross-section of the test-specimen was  $6 \times 14$  mm.

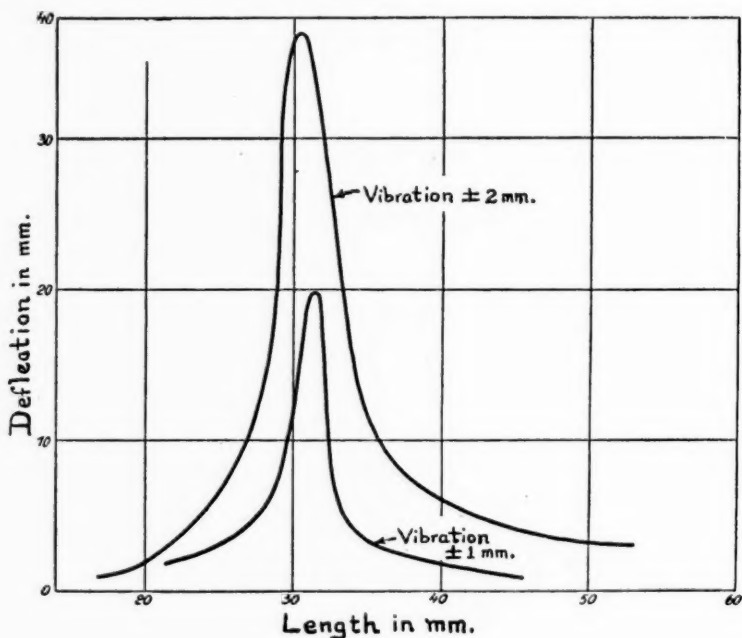


FIG. 3

The base mixtures used for testing natural rubber and Buna-S were as follows:

Buna-S	Buna-S (Defo hardness 600)	100
	Sulfur	1.8
	Vulkacit	1
	Stearic acid	1.5
	Naftolen-ZD	4
	Zinc oxide	2
Natural rubber	Smoked sheet	100
	Sulfur	3
	Vulkacit-DM	0.7
	Stearic acid	1.5
	Naftolen-ZD	4
	Zinc oxide	2

The tabulated results in Table 1 make evident certain facts.

TABLE 1

Type of rubber	Filler	Percentage (by vol.)	Density	EB (kg. per sq. cm.)	EZ (kg. per sq. cm.)	Stress at 300% elongation (kg. per sq. cm.)	Hardness (Shore)	Softness (DVM)	ED (kg. per sq. cm.)
Smoked sheet	Zinc oxide	10	1.37	12.4	8.9	24.5	44	87	36
		20	1.70	16.5	15	39	50	71	39
		30	2.02	40.5	19.2	57	58	58	61
		40	2.26	43.5	24.5	66	64	47	74
Buna-S		10	1.41	23.5	10.2	16	50	80	39
		20	1.77	37.5	13.2	19	58	62	56
		30	2.10	50.3	16.5	22.5	62	52	76
		40	2.32	81	19.5	27	67	44	96
Smoked sheet	Magnesium carbonate	10	1.08	18.2	11.6	24.5	44	65	36
		20	1.16	28.8	13.8	32	50	60	42
		30	1.25	35.8	15.6	38	50	54	48
		40	1.31	51	19.4	48	53	46	56
Buna-S		10	1.09	35.6	13.4	20.0	52	60	50
		20	1.20	52	19.2	26.5	60	56	64
		30	1.28	83.3	23.5	32	63	54	83
		40	1.34	100	26	32.5	68	49	108
Smoked sheet	Carbon black (Luv. 36)	10	1.04	10.5	8.3	24.5	42	88	33
		20	1.11	16.8	11.8	42	48	80	36
		30	1.16	21.1	14	61	54	65	44
		40	1.21	41	18.8	82	59	56	65
Buna-S		10	1.06	30.0	10.3	25	51	74	43
		20	1.13	35.7	13.2	38	56	65	52
		30	1.18	55.5	13.8	39	59	57	54
		40	1.24	76	19.6	73	65	55	74
Smoked sheet	Carbon black (P-1250)	10	1.03	21.5	11.2	31.5	49	58	42
		20	1.10	53	16.4	57	60	44	69
		30	1.14	160	23	98	70	36	138
		40	1.19	347	37	112	78	27	241
Buna-S		10	1.06	37.0	21.5	68	55	65	45
		20	1.11	76.0	26	93	63	49	80
		30	1.16	182	27.5	99	73	33	121
		40	1.21	360	45	140	81	25	203
Smoked sheet	Carbon black (Kosmos)	10	1.05	18	8.1	23.5	41	92	33
		20	1.10	36.8	11.2	40	51	66	46
		30	1.16	65	17	71	58	63	54
		40	1.21	195	31	110	73	42	108
Buna-S		10	1.07	43.7	11	22.5	55	64	49
		20	1.12	82	21	52	65	53	87
		30	1.17	174	21.5	64	72	47	125
		40	1.22	340	32	86	80	34	137

There is no parallelism between the tensile values and dynamic values, nor between the compression values and dynamic bending values. The dynamic-bending values for all inactive fillers lie between the tensile values and compression-modulus values. On the other hand, with the higher percentages of active carbon black, the dynamic-bending values are greater than the compression-modulus values. This is attributable to the fact that the elastic properties depend on the frequency of bending.

As is known, active fillers have a damping effect, because they increase the internal friction of the rubber mixture and thereby increase the time of relaxation. This results in turn in a greater increase in the elastic modulus with increase in frequency, as in the case of inactive fillers.

A more evident relation is found between the hardness and dynamic-bending modulus.

Figure 4 shows the relation between hardness and bending modulus; Figure 5 shows the relation between softness (DVM) and bending modulus.

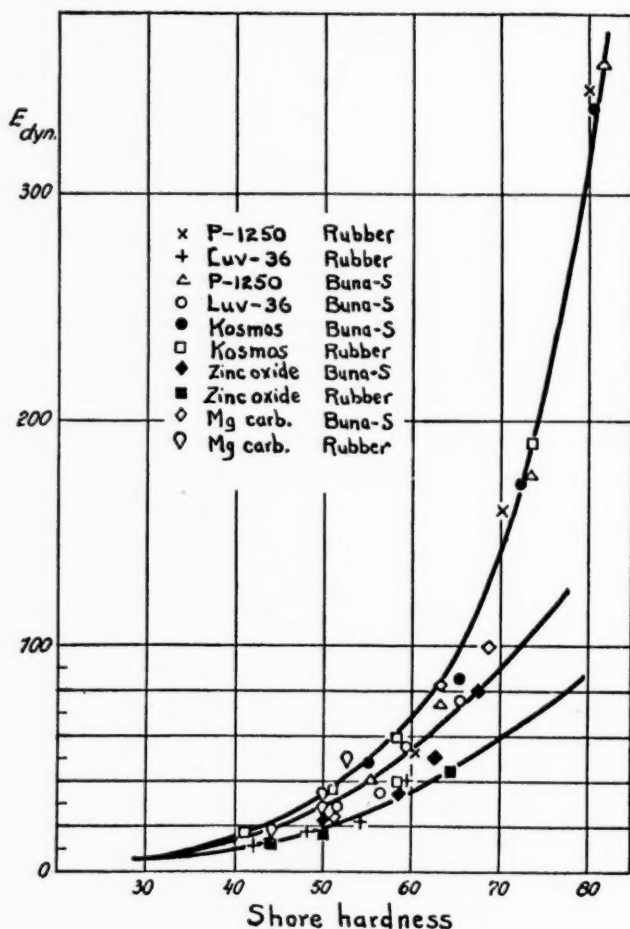


FIG. 4

In these particular measurements the DVM softness gave the less consistent values.

It is evident that there is an area of plotted values between two limiting curves, and that the most active fillers lie either on or near the upper limiting curve, while the less active fillers lie on or close to the lower curve. This

general behavior was found to be true of both natural rubber and Buna-S. The stiffness of a vulcanized rubber product when bent by vibrations of high-frequency is not, therefore, by any means a function of hardness alone, but depends to a great extent on the character of the filler as well.

The method described in the present paper requires no greater expenditure of time for making a single measurement than does a measurement of the DVM

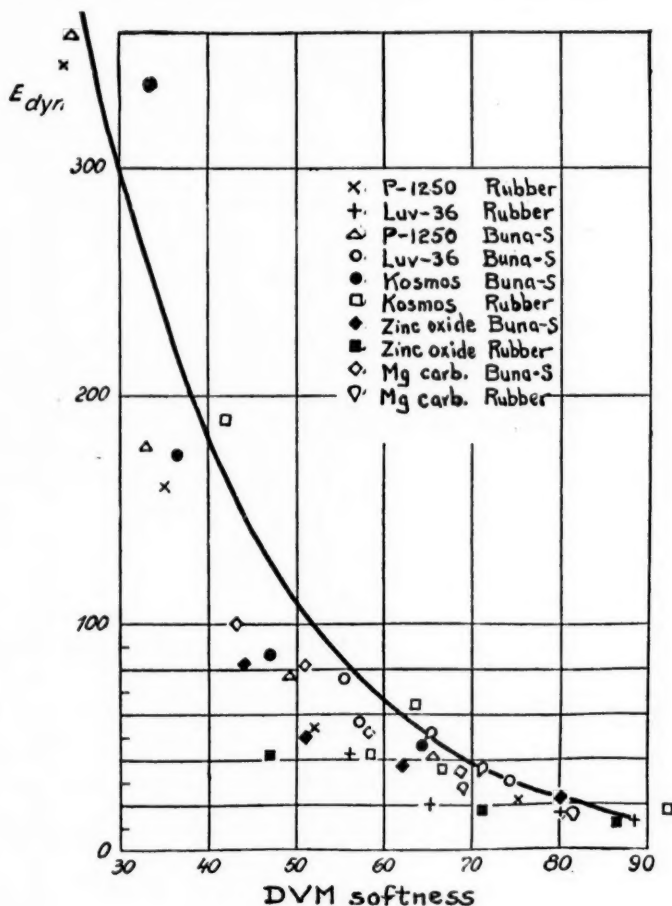


FIG. 5

softness, and only the evaluation requires a longer time. Application of the method to both hot and cold testing is possible without great expense.

#### MATHEMATICAL SUPPLEMENT

The differential equation of the vibration is:

$$IE_B \frac{\delta^4 y}{\delta x^4} = \rho \cdot F \cdot \omega^2 (y + e)$$



with the limiting conditions that (1)  $x = 0$ ;  $y = 0$ ;  $y' = 0$  (fixed attachment), and (2)  $x = l$ ;  $y'' = 0$  (no moment of rotation at the free end);  $y''' = 0$  (no stress at the free end).

$E_B$	elastic modulus of bending
$I$	moment of inertia (sq. cm.)
$\rho$	density
$F$	cross-sectional area
$y$	deflection at point $x$
$e$	vibration at the point of attachment (cm.)

The solution of the problem is then:

$$y = \alpha \sin kx + \beta \cos kx + \gamma \sin kx + \delta \cos kx - e$$

By introducing the limiting conditions in this equation and making certain simple conversions, the following equation is obtained, in which  $s = \sin kl$ ,  $c = \cos kl$ ,  $S = \sin kl$ , and  $C = \cos kl$ :

$$y = e \left\{ \frac{sC + cS}{2(cC + 1)} (\sin kx - \sin kx) - \left\{ \frac{c}{c + C} + \frac{(sC + cS)(s + S)}{2(cC + 1)(c + C)} (\cos kx - \cos kx) + \cos kx - 1 \right\} \right\}$$

In this case no account is taken of the damping effect.

The deflection is infinite if

$$cC + 1 = 0$$

Therefore

$$\cos kl \cdot \cos kl = -1$$

The lowest frequency for which this is the case is:

$$\omega = \sqrt{\frac{IE_B}{\rho F}} \left( \frac{\beta^2}{l_r} \right)$$

With a rectangular cross-section:

$$\omega = \frac{h}{l_r^2} \sqrt{\frac{E_B}{\rho}}$$

For a frequency of 50 Hertz units, the dynamic bending modulus is calculated to be:

$$E_B = 0.098 \cdot \rho \cdot \frac{l_r^2}{h^2}$$

where  $l_r$  is the resonance length in cm.,  $\rho$  is the specific gravity, and  $h$  is the thickness in the direction of vibration.

The curvature of the test-specimen at the point of attachment when the deflection is at its maximum, and thereby the bending stress, can be calculated in an approximate way by means of the following relation:

$$\frac{1}{R} \approx \frac{3.4y}{l_r^2}$$

## A NEW METHOD FOR DETERMINING THE RESISTANCE OF SOFT-RUBBER PRODUCTS TO LOW TEMPERATURES \*

J. AENGENEYNDT AND W. KESTERNICH

When cooled to temperatures below  $0^{\circ}\text{C}$ , every type of vulcanized rubber, no matter how highly elastic it may be at room temperature, first becomes leathery and finally completely hard. This phenomenon must be taken into consideration in the performance of various rubber products, especially automotive parts and products used for military purposes, and consequently care must be taken that rubber parts are designed to be still serviceable, *i.e.*, show satisfactory resistance to cold, at the temperatures to which they are exposed in service.

For obvious reasons the problem of cold resistance has in recent years become of increasing importance, and there has arisen the need for an apparatus which is easy to operate, and for a simple testing method to determine resistance to low temperatures. The present paper deals with a new apparatus which has been devised for testing finished rubber parts, and which can be used for testing products of all types.

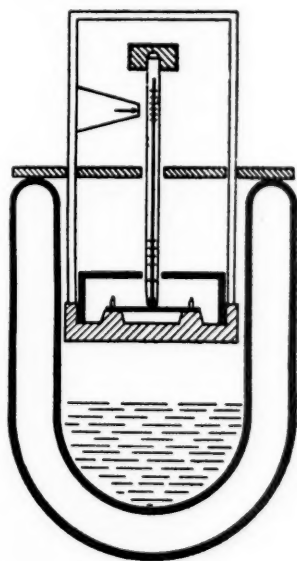


Fig. 1

This apparatus is illustrated schematically in Figure 1. It consists of a double-walled vessel which is partly filled with liquid air. The test-specimen

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 20, pages 1-2, January-February 1944.

is in the form of a strip, approximately 60 mm. long, 10 mm. wide, and 1-2 mm. thick, prepared from the rubber product to be tested. This test-specimen is fastened under slight tension between two supports, and is then covered by a casing. A low-temperature thermometer rests on the middle of the test-specimen<sup>1</sup>. This thermometer carries on its upper end a scale graduated in millimeters.

In making a determination, the frame with the test-specimen and the thermometer are held at a definite distance from the surface of the liquid until the thermometer reads the desired temperature with sufficient constancy. A weight is then placed on the top of the thermometer, and the resulting bending of the test-specimen is read on the scale at the top of the thermometer<sup>2</sup>. It can be shown in this way that the flexure of a test-specimen depends on the temperature and on the behavior of the specimen at low temperatures. This relation between deflection and temperature is illustrated in Figure 2 for one particular type of vulcanized rubber.

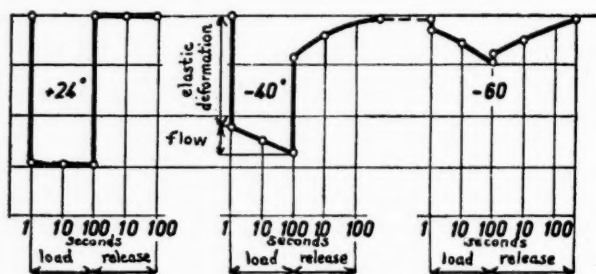


FIG. 2

Following the procedure chosen by Roelig<sup>3</sup>, the deflection was measured after various time intervals from the moment of application of the load, *viz.*, after 1, 10 and 100 seconds. Measurements were then made of the deflection remaining after various times following removal of the load on the test-specimen.

As is evident, the rubber strips tested in the present work behaved, when at room temperature, approximately like steel, *i.e.*, the immediate deflection which was caused by a load did not increase appreciably as long as the load was applied, and when the load was removed, the rubber recovered almost immediately its original form. On the contrary, at  $-40^{\circ}\text{C}$ , two phenomena were evident; first, an elastic deformation, and secondly a flow which took place during the period from 1 to 100 seconds after application of the load. After removal of the load, a similar phenomenon was observed. When the temperature was  $-60^{\circ}\text{C}$ , the elastic deformation was very small directly after application of the load, whereas there was considerable flow subsequently. Corresponding changes were observed after removal of the load.

The actual procedure was that shown in Figure 3a, which shows the deflection as a function of the temperature after the load had been applied for 10 seconds. Between  $20^{\circ}\text{C}$  and  $-20^{\circ}\text{C}$  there was little or no change in the deflection, but below  $-20^{\circ}\text{C}$  the deflection decreased progressively down to about  $-65^{\circ}\text{C}$ . At  $-65^{\circ}\text{C}$ , the load caused no appreciable deflection, for at this temperature the rubber had become completely hard.

By changing the experimental conditions, but with the same sample of rubber, a different curve was obtained. The load was doubled and the pre-

liminary extension of the rubber strip was increased from 2 to 10 per cent. The course of this second curve is similar to that of the first, and confirms the fact observed in the first experiment, *viz.*, that there were no fundamental changes in the properties of rubber from room temperature down to about  $-20^{\circ}\text{C}$ , but that at temperatures lower than this, the rubber stiffened noticeably, and finally became hard at  $-65^{\circ}\text{C}$ .

The character of these curves makes it clear that the experimental conditions, particularly the magnitude of the stress, did not in themselves have any influence on the results. The curve in Figure 3c illustrates especially clearly the behavior of rubber within the temperature range investigated. Down to temperature  $t_1$  the rubber was completely elastic; between temperatures  $t_1$  and  $t_2$  it was leathery, and below temperature  $t_2$  it was hard. On a basis of these three physical states, it is possible to characterize in a simple yet well defined way the behavior of any type of vulcanized rubber at low temperatures.

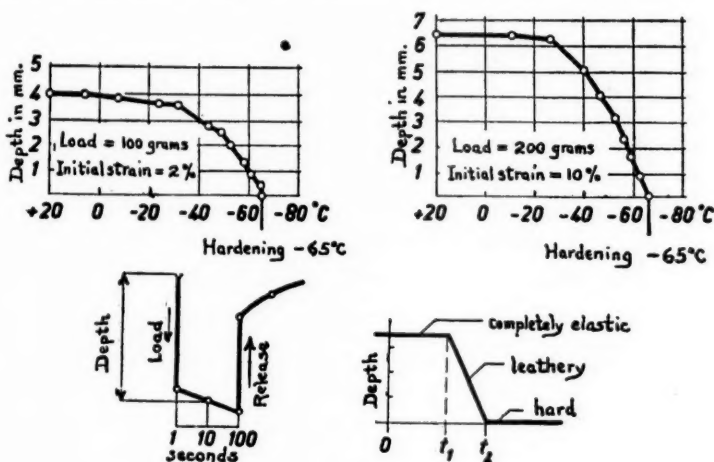


FIG. 3

The apparatus is shown in detail in Figure 4. As is evident from the illustration, five test-specimens can be tested side by side. The cold thermometer is inserted through a perforated Plexiglass disc, so that it is possible to observe the test-specimens throughout the tests.

The apparatus is simple to construct, and because of the avoidance of complicated measuring devices, it is always possible to check the hardening point, in general a particularly important property, not only by the noticeable stiffening or hardening, but also by the ringing sound of the thermometer when it is allowed to hit the taut test-specimen. This makes possible a rapid method of testing, in which no curves are plotted, and the evaluation of the sample is extremely simple, since it involves merely a determination of the stiffening point, which can be determined without recourse to graphical or other technical methods, but which can be checked very easily, if desired, by these methods.

As a means of estimating the serviceability of a particular type of rubber product at low temperatures, the increase in the dynamic elastic modulus with lowering of temperature is especially worthy of consideration. In this case

the two methods to which reference has already been made<sup>4</sup> can be used to obtain quantitative data on these changes in modulus. On the other hand the method described in the present paper is intended primarily as a means of determining the temperature at which a rubber product becomes hard, for this temperature gives an indication of the lowest temperatures at which a rubber product is still serviceable.

The difference between the hardening temperature and the temperature to which the product is exposed in service depends on the character of this service. In the case of products which are in motion at the lowest operating temperature, e.g., hose, the hardening temperature should be 15° C below the operating

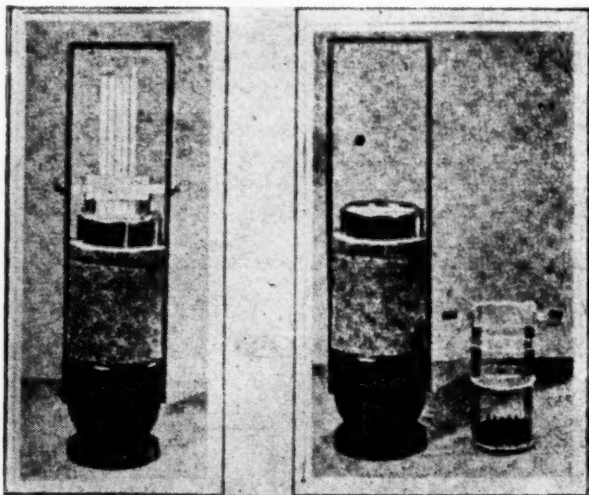


FIG. 4

temperature, whereas in the case of products which undergo little or no motion, e.g., packing, this temperature difference need not be greater than 5° C.

#### SUMMARY

A simple method for testing the behavior of vulcanized rubber at low temperatures is described. In this method test-specimens in the form of strips prepared from finished goods, such as packing, hose, etc., are tested by a simple technique, without the necessity of mathematical calculations or the plotting of graphs.

It is recommended that the hardening point be used as a criterion of behavior of vulcanized rubber in service at low temperatures, i.e., its resistance to cold. When this method is used, this hardening temperature should be 5° to 15° C below the lowest outside temperature at which the particular product must still operate satisfactorily.

#### REFERENCES

- <sup>1</sup> If more precise measurements are desirable, a thermocouple can be used instead of a thermometer.
- <sup>2</sup> Koch, *Kautschuk* 16, 151 (1940).
- <sup>3</sup> Roelig, *Kautschuk* 18, 1 (1942).
- <sup>4</sup> Koch, *Kautschuk* 16, 151 (1940); Roelig, *Kautschuk* 18, 1 (1942).

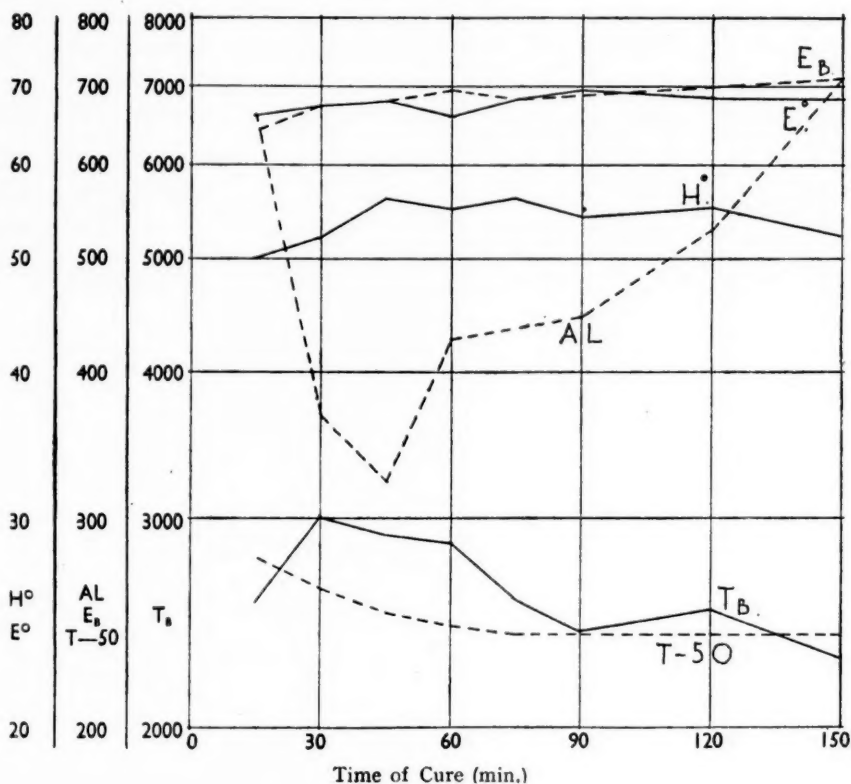
## COMPARISON OF ABRASION RESISTANCE WITH OTHER PHYSICAL PROPERTIES \*

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The measure of the curing rate of rubber stocks has, for many years, been based on tensile strength values or factors involving tensile strength.

From these data, a number of rubber stocks have been termed flat-curing, but if the rate of cure be related to the resistance to abrasion, the stocks would not be regarded as possessing that property.



It appears that the abrasion test is more sensitive to changes in the state of cure than the tensile strength test, and it is therefore suggested that curing rates should be based on abrasion test data.

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 20, No. 3, pages 101-102, October 1944.

To illustrate this claim, the following mix was prepared:

TABLE I

Rubber	44.64
Whole-tire reclaim	9.70
Sulfur	2.18
Accelerator	0.21
Zinc oxide	24.26
Stearic acid	0.61
Antioxidant	0.55
Pine tar	0.48
Pitch	2.91
Clay	14.46
	<hr/> 100.00 <hr/>

The resulting stock was cured for the times stated (Table 2) and each vulcanizate was tested for hardness ( $H^\circ$ , Shore reading), elasticity ( $E^\circ$ , Shore reading), T-50 (degrees absolute), tensile strength ( $T_B$  lb. per sq. in., Scott Testing Machine), elongation at break ( $E_B$  per cent, Scott Testing Machine), and abrasion loss (A.L. cc. per h.p.-hour, Williams Machine).

TABLE 2

Cure (min.)	$H^\circ$	$E^\circ$	T-50	$T_B$	$E_B$	A.L.
15	50	66	276	2550	640	660
30	52	67	262	3040	670	364
45	56	68	248	2905	680	324
60	55	66	243.5	2860	690	425
75	56	68	239	2560	680	435
90	54	69	238.5	2460	680	445
120	55	68	238	2500	700	529
150	52	68	238	2295	710	705

The result of the tests are given in the Table 2 and are plotted in the diagram. It will be observed that the chart is semilogarithmic. The reason that this type of chart is used is that the percentage change of all curves are then directly comparable without reference to the numerical values.

Curves of the same percentage changes in the results of two series of tests would be identical, whatever their position on the chart.

The diagram shows that the abrasion test is more sensitive to variations in the time of cure than any of the other standard tests.



# FATIGUE FAILURE OF GR-S TREAD STOCKS\*

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The fundamental nature of fatigue failure in rubber during flexing has been widely studied and is known to be complex. Among the more important factors involved (aside from variations in compounding) are state of cure, temperature of test, and oxidation. The object of this paper is to review and extend these studies as they apply to GR-S.

Several investigators<sup>1</sup> have studied the effect of time of cure on the flex cracking resistance of rubber. Busse<sup>2</sup> found that, as the degree of cure was advanced, the flex resistance reached a maximum and then decreased. Similar studies on GR-S<sup>3</sup> show that undercures flex better than either normal cures or overcures. Prettyman<sup>4</sup>, using a different type of machine, showed a maximum near the optimum cure.

Cadwell, Merrill, Sloman and Yost<sup>5</sup> and Rainier and Gerke<sup>6</sup> report that the rate of cracking of rubber increased with the temperature of flexing. Similar results have been demonstrated with GR-S by Breckley<sup>7</sup> and by Carlton and Reinbold<sup>8</sup>.

Neal and Northam<sup>9</sup> flexed rubber in air, oxygen, and nitrogen on a du Pont type flexing machine. They report no difference between the flexing behavior in air and oxygen. In nitrogen, however, an uninhibited stock flexed five times longer than in air before any failure was evident. The presence of an anti-oxidant did not change the behavior in nitrogen, but doubled the normal flex-life in air. These workers concluded that the failure of rubber on flexing is due to oxidation rather than to mechanical fatigue. No comparable work on GR-S has yet been reported.

The present authors<sup>10</sup> previously showed that oxygen plays an important part in the hardening of GR-S vulcanizates during accelerated aging tests in the 100° C air oven. Since high temperatures are developed during flexing, which might well result in a similar hardening by oxidation, it seemed desirable to determine whether oxygen plays a part in the flex-cracking of GR-S. For this purpose a typical tread stock was selected and flexed in air and in nitrogen which contained various small percentages of oxygen. The effect of state of cure and testing temperatures on the resistance of GR-S to flex-cracking was included in the study.

## EXPERIMENTAL PROCEDURE

The tread type stock employed in this study was compounded according to the following formula from GR-S, made according to government specifications, and containing approximately 2 parts of phenyl- $\beta$ -naphthylamine:

GR-S	100	Zinc oxide	5
Channel black	50	Sulfur	2
Bardol	5	Santocure	1.2
Fat acid	1.5		

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 37, No. 1, pages 67-70, January 1945. This paper was presented at a Symposium on Synthetic Rubber by the Engineering Section of the American Association for the Advancement of Science, Cleveland, Ohio.

Regulation grooved test-specimens were flexed in a De Mattia type flexing machine. Three specimens were used for each determination.

Vila<sup>11</sup> showed that the growth of an initial cut is more reproducible than measurements of flex-life on unnicked specimens. The present authors employed an automatic lance for the initial cut to ensure uniformity. The resulting nick was approximately 0.035 inch in length. In most of the work a duplicate set of unnicked specimens was run simultaneously to determine the number of flexures required both for the appearance of the first crack and for this crack to progress completely across the one-inch specimen width. These values are reported in the tables under the headings "appearance of first crack", "first crack to failure", and "total to failure". In all cases "failure" was taken as that point at which the crack had progressed completely across the groove.

When the variation between individual test-specimens exceeded a few thousand flexes, the average maximum difference is indicated in the tables. This number was obtained by dividing the maximum difference between specimens by the number included in the average.

The flexing machine was enclosed in a case both for testing at elevated temperatures and in nitrogen atmospheres, as shown in Figure 1. Strip

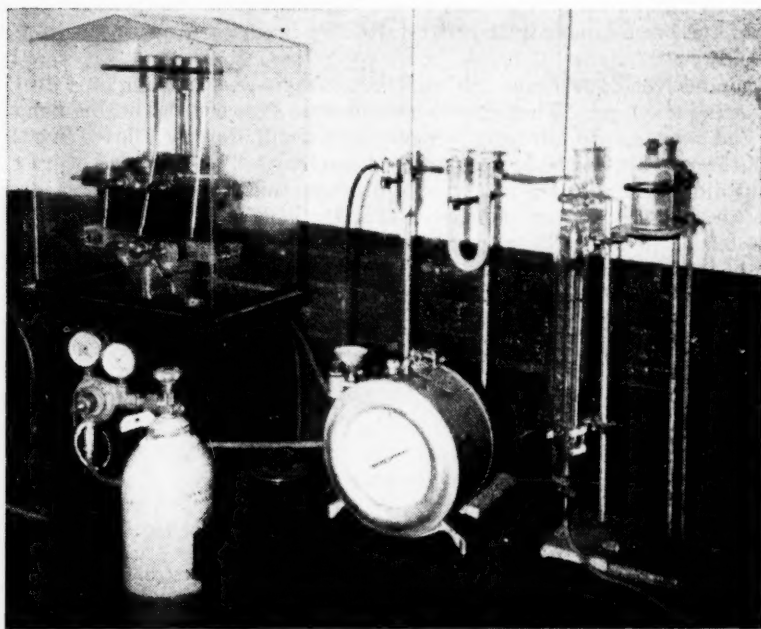


Fig. 1.—Flexing machine equipped for testing in nitrogen.

heaters and a fan were mounted inside the cabinet to maintain the desired temperature. Thermometers mounted at specimen level were used to measure the temperature of the test.

For those experiments in which a reduced oxygen concentration was employed, nitrogen of appropriate purity was passed through the cabinet at a

constant rate, and analyses of the exit gas for oxygen were made at frequent intervals by an adaptation of the Winkler method<sup>12</sup>. The average oxygen content reported for the test is the mean of the separate analyses made during the test. An oxygen content of approximately 1 per cent by volume was obtained by passing commercial nitrogen through the cabinet at a rate of 0.25 cubic foot per minute. A purified nitrogen, analyzing 0.08 per cent oxygen and passing at a rate of 0.3 to 0.4 cubic foot per minute, gave an average content of 0.4 per cent oxygen; a rate of 1 cubic foot per minute reduced the average content to 0.2 per cent. For still lower oxygen contents it was found desirable to employ a specially prepurified nitrogen, supplied by the General Electric Company, containing less than 5 parts per million of oxygen. Using this nitrogen at a rate of 1 cubic foot per minute, the average oxygen content of the exit gas was 0.05 per cent by volume. Since this was sufficiently low to show a definite effect on the flexing results, no attempt was made to reach a lower value.

All samples which were to be flexed in nitrogen, together with their controls, were placed (immediately after vulcanization) in a desiccator over alkaline pyrogallol so as to remove, in so far as possible, the oxygen from the surface of the samples.

#### STATE OF CURE

The flexing data for four different cures, including a marked undercure and an overcure, are presented in Table I and plotted in Figure 2. In the case of

TABLE I  
EFFECT OF STATE OF CURE ON FLEXING

Cure (min. at 298° F)	No. of Flexures in Thousands			
	Initial cut to failure	To appearance of first crack	First crack to failure	Total to failure
15	77	42 ± 5	<sup>a</sup>	<sup>a</sup>
30	12	7 ± 4	18 ± 5	25 ± 6
50	8	3	13	15
80	8	3	8	11

<sup>a</sup> One of the three strips failed at 85,000; one was half failed and the third was one-third failed after 100,000 flexes.

the unnicked 15-minute cure specimens, the test was terminated after 100,000 flexes; at that point two of the samples were only one-half and one-third failed, respectively. One had failed at 85,000 flexes. The dashed portions of the curves in Figure 2 are estimated from the degree of failure at 100,000 and measured rates of crack growth.

The curves show that GR-S has good flexing resistance when undercured, but that, as the cure is advanced, the flex resistance decreases rapidly and levels off at what is frequently considered an optimum cure. An overcure, however, produced little additional change in the flexing resistance. These results are consistent with those obtained by the workers previously cited.

Although Gehman, Jones and Woodford<sup>13</sup> did not measure flex cracking directly, they showed that for both rubber and GR-S the heat generation during flexing under compressive load at constant deflection starts with a lower value for an undercure, and approaches a limiting value as time of cure increases. The lower temperature rise for the undercure may account in part for the better flexing properties. Another factor may be the small amount of flow or perma-

ment set, which results in a lower stress during the testing of an undercured sample.

### TESTING TEMPERATURE

The result of flexing identical samples at four different temperatures is shown in Table II. These data are plotted as the log of the number of flexures

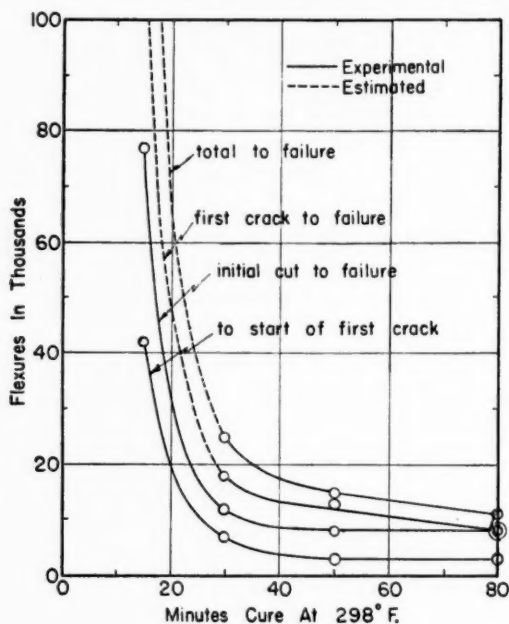


FIG. 2.—Effect of cure.

against testing temperature in Figure 3. Inasmuch as crack-growth data are

TABLE II  
EFFECT OF TESTING TEMPERATURE ON FLEXING (50-MINUTE CURE AT 298° F)

Temp. of test (° C)	No. of Flexures in Thousands			
	Initial cut to failure	To appearance of first crack	First crack to failure	Total to failure
23	30 ± 4	6	48 ± 8	54 ± 8
40	17	5	32	37
60	10	3	18	21
80	7	2	8	10

most reproducible, the straight lines drawn through the various points for the other measurements are parallel to the best straight line through the points representing the crack growth data.

It is evident that testing temperature is an important factor, and that the higher the temperature, the poorer the flexing properties become. The temperature coefficient obtained from the lines of Figure 3 is 1.3 per 10° C change in temperature over the range 20° to 80° C.

Although no values for this particular temperature coefficient have been reported previously, calculations based on the data of Carlton and Reinhold<sup>8</sup>

show a temperature coefficient for this change of 1.5 per  $10^{\circ}\text{C}$  change over a range of approximately  $25^{\circ}$  to  $80^{\circ}\text{C}$ . An estimate of the coefficient based on the work of Breckley<sup>7</sup> is 1.3 to 1.5 per  $10^{\circ}\text{C}$  between room temperature and  $100^{\circ}\text{C}$ . The agreement is good, especially when it is remembered that Carlton and Reinhold used a du Pont type machine, whereas Breckley and the present authors used a De Mattia type.

A coefficient of 1.3 would indicate a rather low energy of activation for a simple chemical reaction. Although a chemical reaction may be included in

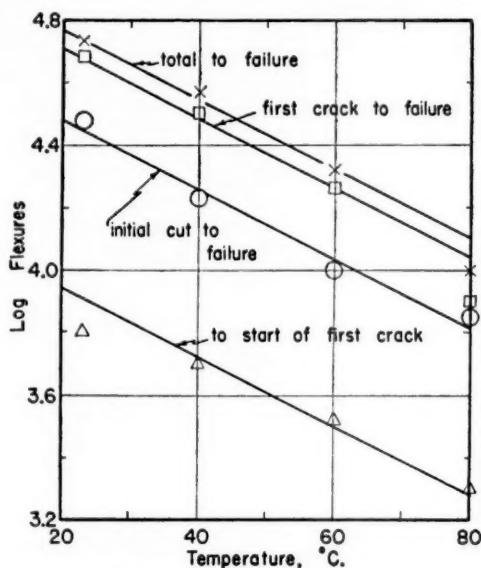


FIG. 3.—Effect of testing temperature.

this change, other factors (physical in nature) would appear to be rate determining.

#### FLEXING IN AIR AND NITROGEN

The effect of oxygen on the flex-cracking rate of GR-S is shown in Table III.

TABLE III  
EFFECT OF OXYGEN CONCENTRATION ON FLEX LIFE

Flexed in	Oxygen concn., (% by vol.)	Temp. (° C)	No. of Flexures in Thousands				Cure (min. at 298° F) Shore hardness	
			Initial cut to failure	Appearance of first crack	First crack to failure	Total to failure		
Air	...	27	11	...	...	...	40	64
N <sub>2</sub>	1.0	30	9	...	...	...	...	...
Air	...	27	10	...	...	...	40	64
N <sub>2</sub>	1.0	30	9	...	...	...	...	...
Air	...	29	15	5	21	26	30	61
N <sub>2</sub>	0.37	30	15	7	19	27	...	...
Air	...	30	23	13	27	40	25	57
N <sub>2</sub>	0.21	30	30	18 ± 7	40 ± 5	58 ± 12	...	...
Air	...	30	22	7	35	42	30	59
N <sub>2</sub>	0.05	30	28	12	55	67	...	...

In each case identical samples were flexed, one set in air and the other in nitrogen having the appropriate oxygen content. Duplicate batches were run at the

1 per cent oxygen level to show the reproducibility of results. No improvement in flexing characteristics was found at this oxygen concentration.

A different lot of GR-S was employed for the last three batches. This difference is reflected in both the hardness and flexing data. Small differences in cure also make it impossible to compare the different control samples directly. Since each batch had its control run in air, these variations do not affect the validity of the results from the standpoint of the effect of oxygen concentration upon flex cracking.

No uninhibited stock was included in this series. It has been repeatedly demonstrated in this laboratory, however, that the presence or absence of the antioxidant, phenyl- $\beta$ -naphthylamine, makes little difference in the flexing results obtained in air, and consequently none would be expected in nitrogen. A typical example from these unpublished data is presented in the following tabulation; the uninhibited polymer was prepared in the manner previously described<sup>10</sup>:

	Uninhibited GR-S tread stock	Same stock with 2 parts antioxidant
No. of flexures in thousands		
Initial cut to failure	10	13
To appearance of first crack	9	13
First crack to failure	19	25
Total to failure	28	37
Cure at 298° F (min.)	25	30
Shore hardness	58	57

The small difference in flexing behavior noted here may be attributed to the difference in cure resulting from the slower curing rate of the inhibited stock. In other cases in which the inhibited stock was cured long enough to give a slightly higher cure, the crack-growth value was actually lower than for the uninhibited stock. Similarly, the inclusion of 5 additional parts of antioxidant in a GR-S stock failed to affect the flexing results.

This failure of phenyl- $\beta$ -naphthylamine to affect the flexing resistance of GR-S is in contrast to the behavior with natural rubber<sup>9</sup>. This difference may be explained in part by the much shorter duration of the test resulting from both the poorer flexing resistance of the GR-S and the type of flexing machine employed.

The percentage improvement in flexing resistance obtained by flexing in an atmosphere low in oxygen compared to that in air is shown in Table IV. Since

TABLE IV  
IMPROVEMENT IN FLEX RESISTANCE IN LOW-OXYGEN ATMOSPHERE

Oxygen content (% by vol.)	Percentage Improvement in:			
	Initial cut to failure	To appearance of first crack	First crack to failure	Total to failure
0.37	0	0	0	0
0.21	30	39	48	45
0.05	27	70	57	60

the flex-life was the same with 0.4 per cent by volume of oxygen as with air, whereas 0.2 per cent showed a definite improvement, the critical oxygen content would seem to be about 0.3 per cent. At the lowest oxygen content obtained, 0.05 per cent, still greater improvement was noted in the total flex-life, although the resistance to the growth of an initial cut showed no additional improvement. Apparently, then, in a completely oxygen-free atmosphere, still greater improvement would be obtained.



Although an improvement of 60 per cent falls far short of that required to make a GR-S stock comparable to natural rubber, these results do show that, even in the relatively small time required for the De Mattia flexing test, oxygen reacts with GR-S at a sufficiently rapid rate to affect the results markedly. With a less drastic test—for example, in actual service—more time would be available for oxidation, and the effect on flex resistance would be correspondingly greater. The reaction is probably localized at the points of maximum stress where high temperatures are produced by flexing. This behavior is consistent with the work previously reported<sup>10</sup>, in which it was demonstrated that oxygen played an important part in the hardening of GR-S stocks at elevated temperatures.

#### ACKNOWLEDGMENT

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## THE EVALUATION OF TEAR RESISTANCE IN ELASTOMERS \*

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The need of a tear-resistance test that could be generally accepted by rubber technologists has long been recognized. Although a very common kind of failure in rubber goods, tearing has proved exceedingly difficult to evaluate with the degree of accuracy possible in other physical tests. Perhaps no property of rubber has had a greater variety of tests<sup>1</sup> proposed for its measurement. Lefcaditis and Cotton<sup>2</sup>, in developing one method, investigated the possibilities of at least a dozen specimens which had been devised for this work.

It is not the intention in this paper to review the merits of the many tear-test methods in use or proposed. The work has been confined to a study of the test-specimen coming closest to general acceptance and to a new specimen designed as an improvement on the former. Reference is made to the Goodrich, or Winkelmann, crescent test-piece, which has been in use for more than 16 years and was adopted as tentative standard by the A.S.T.M. in 1941.

The principle of the crescent design is evident on examination of Figure 1. The curved test-section makes possible the development of a stress gradient when the piece is stretched in a tensile machine. Tearing occurs when sufficiently high stress is attained at the apex of a cut, 0.02-inch deep, at the center of the concave edge. The value recorded for tear resistance is expressed as pounds pulled per unit thickness, and is a composite measurement of the stress at the apex of the cut and of other stresses not involved in resistance to tearing.

Tearing has been defined by Busse<sup>3</sup> as the formation of new surfaces by the application of a small force in such a way that it is concentrated at the tip of a sharp indentation, or cut, in the sample. It therefore follows that the ideal specimen would measure the stress concentrated at this point of tearing to the exclusion of all other stresses present in adjacent areas. The values obtained with such a specimen would represent true tear resistance. Unfortunately it has not been practical to develop such a specimen for extensible materials. A compromise has been necessary in which stresses not involved in tear resistance are included in the measurement of the stress at the point of tearing. Because of the composite nature of such measurements, the values obtained with all tear specimens are significant only in a comparative sense. Likewise, values obtained with one type of specimen do not have significance in direct comparisons with values of a different specimen design.

If we consider again Busse's definition of tearing, we must conclude that, lacking the ideal specimen, any specimen to evaluate this property should be so designed that the stress at the point of tearing exerts the dominant influence on the value obtained, while other unavoidable stresses in the specimen are subordinated. This requirement is not met in the crescent specimen. Lefcaditis

\* Reprinted from the *India Rubber World, Natural and Synthetic*, Vol. 111, No. 3, pages 305-308, 317. December 1944.

and Cotton<sup>2</sup> recognized this fault in 1932 when they observed that too great a proportion of the pulling force is distributed throughout the piece, while only a small part is concentrated at the point of tearing.

Because of this distribution of the pulling force, the value obtained at failure is largely a measurement of modulus. The tensional stress reaches its maximum when the tearing stress is attained at the apex of the cut and a pseudo-evaluation of tear resistance is obtained. Under these conditions one would expect a marked relation between the ultimate elongation and the tear values obtained. The data appear to bear this out.

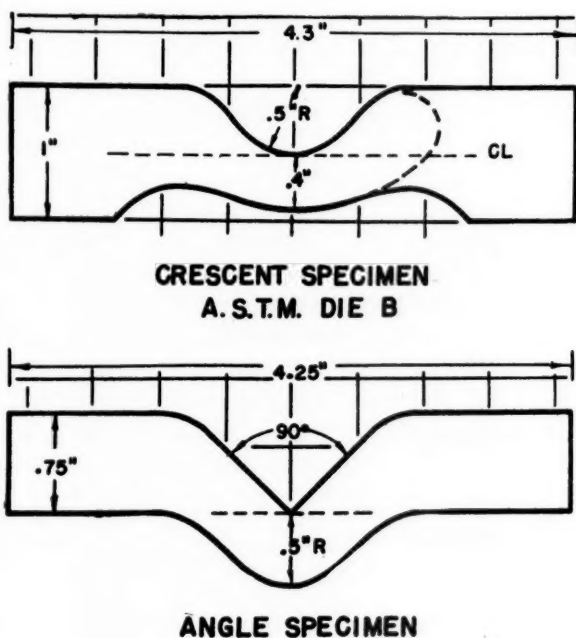


FIG. 1.—Tear test specimens.

Figure 1 also illustrates the specimen designed to meet the requirement suggested above. The crescent test-section is replaced by a 90-degree angle section. The tearing stress is concentrated at the apex of the angle eliminating the need of further nicking. This has resulted in a three-fold improvement in uniformity of data over that obtained with the nicked crescent specimen. In the new specimen the point of tearing has been moved from the center line of pull between the boundary lines of the crescent piece to the boundary line of the angle test-piece (See Figure 1), thus increasing the stress gradient. The result is a tear specimen in which the stress at the point of tearing exerts the dominant influence on the value obtained.

The stress distribution patterns of the two specimens are illustrated in Figure 2, photographed by means of polarized light. The test-pieces were cut from a transparent *Hevea* rubber stock, and each was subjected to a pulling force of one pound. These patterns illustrate how much more effectively the pulling force is concentrated at the point of tearing in the angle specimen.

## EXPERIMENTAL DETAILS

In the following data the two specimens are compared in test compounds of four different elastomers. A study was made of the effect of heat aging (Geer oven at 100° C) on tests at 25° C. In addition the effect of test temperatures on unaged stocks was determined. The compounds were cured and tested following A.S.T.M. procedure except that the tear test-pieces were cut with the grain direction running across the specimen so that tearing would be with the grain.

Carpenter and Sargisson<sup>4</sup> tested seven different compounds of *Hevea* rubber, employing 1,400 test-pieces, and found that with the crescent specimen tearing always followed the grain, regardless of its direction in the test piece. Preliminary tests in this work indicated this characteristic of natural rubber with both specimens. In the synthetic elastomer stocks the effect of grain is not so pronounced, and tearing can be effected across the grain with both specimens. However a slight tendency toward lower tear resistance with the grain was observed.

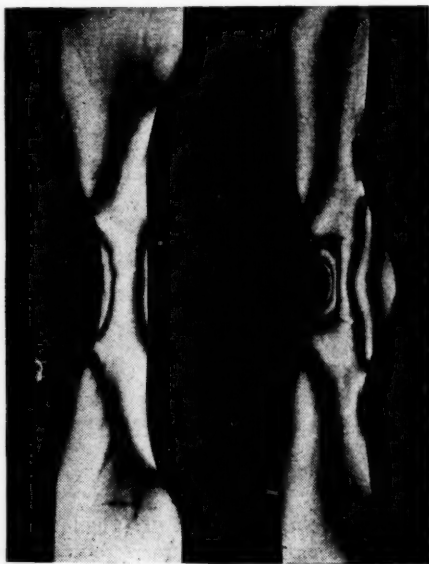


Fig. 2.—Stress distribution patterns as revealed in polarized light; (left) crescent type specimen; (right) angle type.

Some investigators take steps in their mixing and curing procedures to eliminate grain effects. Since this is not a practice followed in commercial processing, it seems unwarranted in the laboratory. If grain from mills and calenders may be present in articles of commerce, and the tendency to tear is in this direction, it seems sound practice to evaluate resistance in this direction in the laboratory. All values given in this paper represent tearing with the grain, and are averages obtained from five specimens in each test.

The oven devised to adapt a Scott tensile machine to testing modulus, tensile, and tear resistance at elevated temperatures is shown in Figure 3.

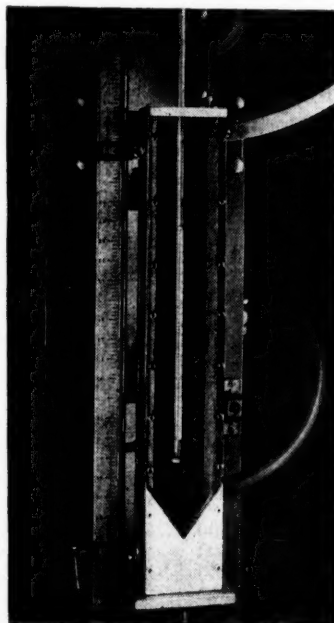


FIG. 3.—Oven equipment for use with Scott tensile machine.

A combination of coil heaters and forced circulation of air insures uniform temperature throughout the test. The oven travels downward with the driven jaw, and elongation is observed through the transparent front. When disconnected from the base, the oven is readily raised and locked by the clamp at the lower guide. In this way free access is had to the jaws for specimen mounting.

TABLE 1

Formulation	Hevea	GR-S	Neoprene	Hycar
Smoked sheet	100			
Buna-S (GR-S)		100		
Neoprene-GN			100	
Hycar OR-15				100
Carbon black (MPC)				50
Carbon black (EPC)	50	50	37	
Zinc oxide	5	5	1	5
Sulfur	3	2		1.25
Stearic acid	3		.5	1
Altax				.8
Captax	.8			
Aero Ac-50	.15			.15
Aero Ac-165		1		
Latac			.5	
L. C. magnesia			4	
AgeRite powder	1.25		2	
Pine tar	2			
Dibutyl phthalate				25
Bardol		5		
Temperature of cure (° C)	141	141	141	153
Minutes (optimum cure)	30	60	30	30

When the oven is again closed, three minutes are allowed to attain temperature equilibrium. Current to the coils is through a standard Variac for temperature control.

The formulation and optimum cures of the test compounds are given in Table 1. The physical data are found in Table 2. The marked improvement

TABLE 2  
EFFECT OF OVEN AGING AT 100° C ON VALUES OBTAINED AT 25° C

Stock tested	Hours at 100° C	Lbs. per Sq. In.		% Elongation at break	Lbs. per 0.1-Inch Thickness			
		At 200% elongation	Tensile strength		Crescent tear	Std. dev.	Angle tear	Std. dev.
<i>Hevea</i>	0	1080	4400	570	65.3	6.3	47.5	2.2
	24	1400	3850	470	69.5	3.5	31.0	1.4
	48	1400	2775	360	47.7	5.6	24.1	.9
	72	1400	2000	260	37.8	3.9	17.3	.2
GR-S	0	835	3100	580	29.4	3.3	22.8	.3
	24	1150	2900	390	24.9	3.1	21.7	.4
	48	1350	2700	320	23.5	3.1	20.1	.6
	72	1500	2600	290	20.1	1.6	18.7	.4
Neoprene	0	1550	3700	450	45.5	5.1	32.9	1.2
	24	1900	3600	345	37.4	2.9	29.1	1.5
	48	2100	3400	310	31.7	1.3	28.5	.9
	72	2100	3400	300	31.0	3.0	26.5	1.3
Hycar	0	995	3800	540	22.7	1.0	20.6	.3
	24	1275	4425	435	23.4	2.9	21.1	.5
	48	1625	4325	380	27.9	1.7	23.3	.3
	72	1950	4250	340	24.5	1.5	22.6	.4

EFFECT OF TEST TEMPERATURE ON ORIGINAL STOCKS

Stock tested	Test temp. (° C)	Lbs. per Sq. In.		% Elongation at break	Lbs. per 0.1-Inch Thickness			
		At 200% elongation	Tensile strength		Crescent tear	Std. dev.	Angle tear	Std. dev.
<i>Hevea</i>	25	1080	4400	570	65.3	6.3	47.5	2.2
	50	1020	3770	600	46.7	3.7	39.9	1.1
	75	880	3360	670	40.7	1.2	38.4	.8
	100	750	2610	650	31.8	.5	35.5	.5
GR-S	25	835	3100	580	29.4	3.3	22.8	.3
	50	750	2260	480	27.8	2.2	19.2	.2
	75	650	1500	380	25.5	1.8	16.0	.5
	100	650	1060	320	23.0	.8	14.9	.5
Neoprene	25	1550	3700	450	45.5	5.1	32.9	1.2
	50	1340	2660	390	38.3	2.1	23.3	.2
	75	1140	1720	290	31.8	2.0	18.6	.2
	100	1080	1420	250	25.5	.7	13.5	.4
Hycar	25	995	3800	540	22.7	1.0	20.6	.3
	50	875	2700	460	19.5	1.8	17.5	.1
	75	830	1470	300	18.2	.9	13.5	.2
	100	820	1130	240	16.5	.6	9.0	.2

Std. Dev. = Standard deviation from mean of five specimens.

in uniformity of test data obtained with the angle specimen is shown in Table 3. The data of Table 2 are plotted in Figures 4 to 7 to show the percentage change

TABLE 3  
COEFFICIENT OF VARIATION OR STANDARD DEVIATION IN PERCENTAGE

Investigation	Test	Crescent Tear Specimen				Angle Tear Specimen			
		Hevea	GR-S	Neoprene	Hycar	Hevea	GR-S	Neoprene	Hycar
Effect of oven aging at 100° C on tests at 25° C	Original	9	11	11	5	5	1	4	2
	24 hours	5	12	8	12	5	2	5	2
	48 hours	12	13	4	6	4	3	3	1
	72 hours	10	8	10	6	1	2	5	2
Effect of test temperature on original stocks	50° C	8	8	5	9	3	1	1	1
	75° C	3	7	6	5	2	3	1	2
	100° C	2	4	3	4	1	3	3	2
Average	7 tests	7	9	7	7	3	2	3	2
Overall variability		7%				2%			

in these properties from the values obtained for the original stocks tested at 25° C.

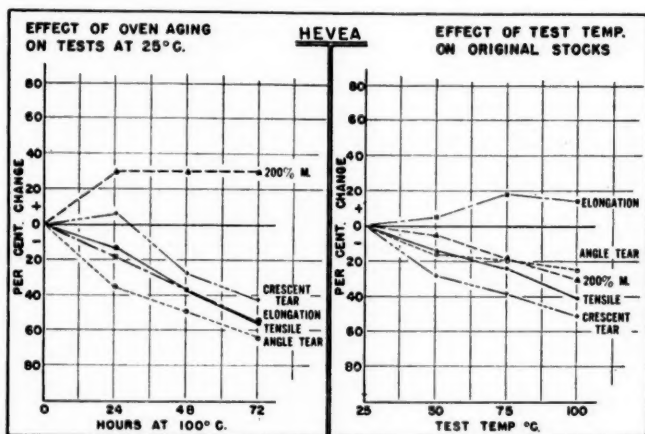


FIG. 4

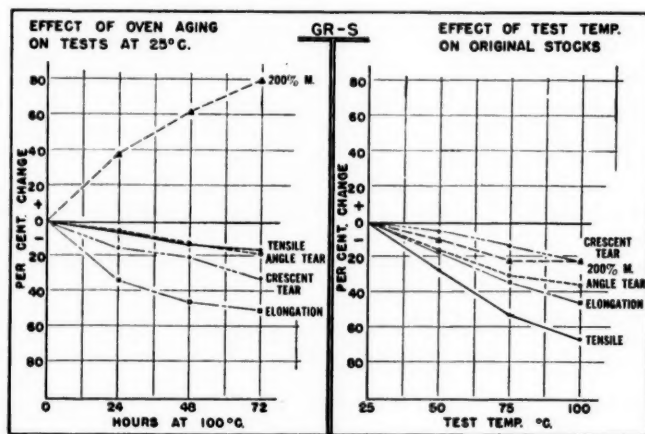


FIG. 5

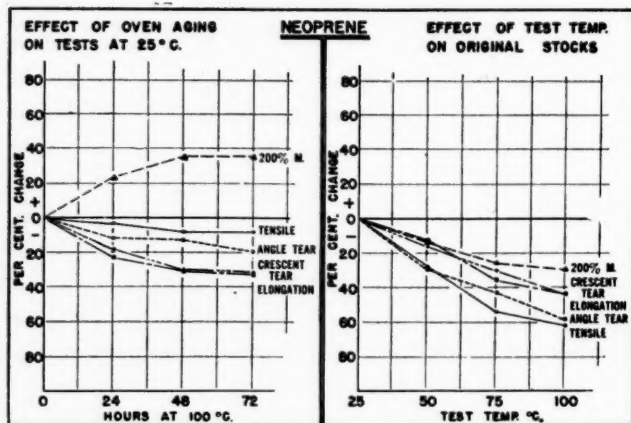


FIG. 6

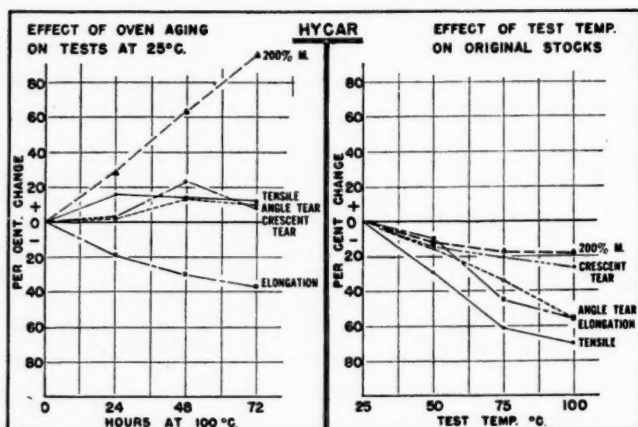


FIG. 7

Before discussing the data reference is again made to the work of Busse<sup>3</sup>. In defining tearing he further observed that in an isotropic material, tearing begins when the stress and strain at the point of tearing reach the tensile strength and ultimate elongation of the material. He then showed that in *Hevea* the tendency to fiber under stress results in a reinforcement of the rubber in the direction of the principal stress, and the force required to cause tearing is not readily correlated with tensile strength. In a synthetic elastomer, such as GR-S, there is no fibering under stress, and the evaluation of tear resistance becomes somewhat less complex.

#### DISCUSSION OF TEST DATA

**HEVEA STOCK (FIGURE 4).**—Referring to Table 2, the value for the original stock is found to be some 37 per cent higher with the crescent specimen than with the angle specimen. Since the crescent specimen has 25 per cent less



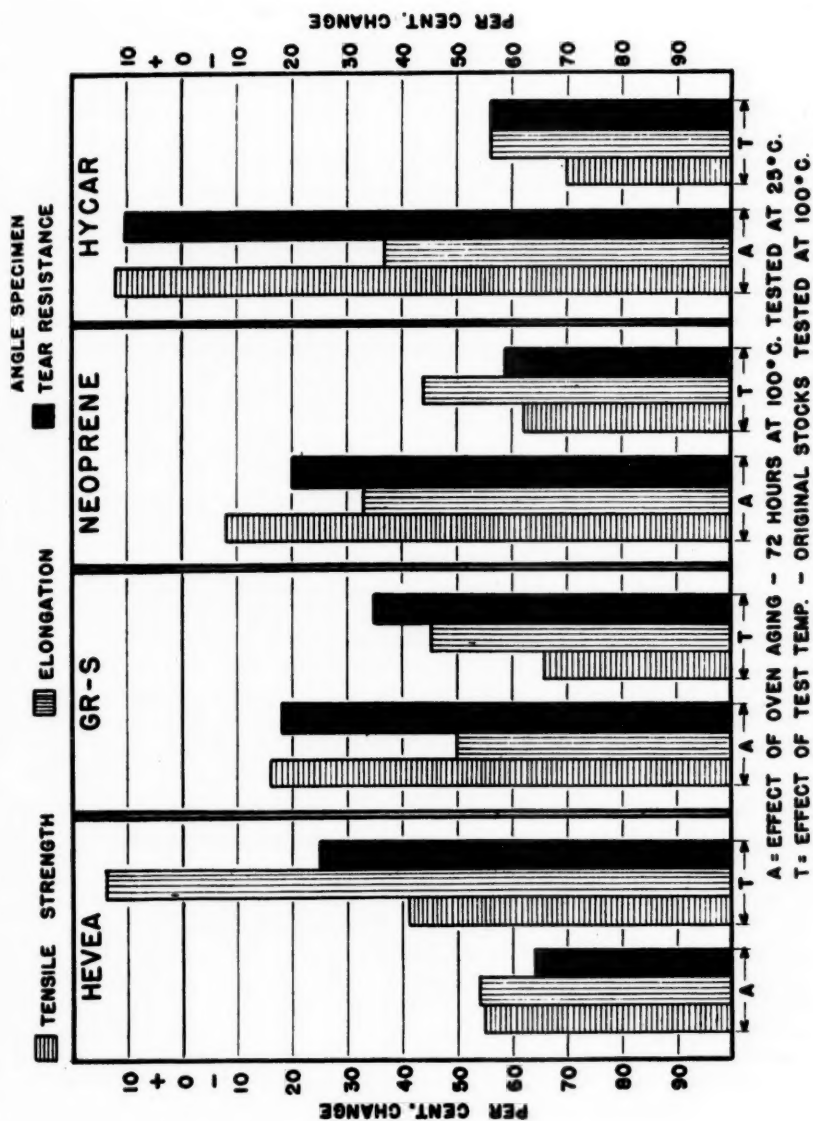


FIG. 8

minimum cross-sectional area, it is evident that the piece is in a higher state of general stress when tearing is effected. Since fiber ing is highly advanced, the influence of modulus on the tear value becomes very marked.

The crescent specimen indicated that, with oven aging (increased modulus), the degradation of tear resistance was less than when the original stocks were tested at elevated temperatures (decreased modulus). The angle specimen indicated that, with oven aging (greater tensile drop), the degradation of tear resistance was greater than with tests at elevated temperature (smaller tensile drop).

An interesting example of the excessive influence of stresses not involved in tearing can be found in the value obtained with the crescent specimen after 24 hours' oven aging. An increase of 6 per cent was indicated while the angle specimen indicated a drop of 35 per cent. This trend was observed in earlier work.

GR-S (Figure 5).—As there is no tendency to fiber under stress in GR-S, a clearer picture of the factors influencing tear resistance can be drawn. The crescent specimen indicated that, with oven aging (greater drop in elongation), the degradation of tear resistance was greater than when the original stocks were tested at elevated temperatures (small drop in elongation). The angle specimen indicated that, with oven aging (smaller tensile drop), the degradation of tear resistance was less than with tests at elevated temperatures (greater tensile drop).

NEOPRENE (FIGURE 6).—The influence of elongation on the crescent tear values and of tensile strength on angle tear values is at once evident. When test conditions cause elongation to drop more than tensile strength, the crescent values drop more than the angle values and *vice versa*.

HYCAR (FIGURE 7).—In this compound the effect of oven aging on physical properties is complicated by the presence of a fugitive plasticizer at 25 per cent concentration. As the plasticizer is volatilized, there is an increase in tensile strength and tear resistance as reflected by both specimens. Apparently the dominating effect on tear resistance came from the combination of modulus increase and tensile increase.

Data on tests at elevated temperatures indicated again that, with tensile strength dropping more than elongation, angle tear values dropped more than crescent values.

The percentage change in tensile strength, elongation, and tear resistance, as evaluated by the angle specimen, is recapitulated in bar chart form in Figure 8. The synthetic elastomers tested show less degradation of tensile strength and tear resistance than *Hevea* rubber with oven aging at 100° C. In tests on the original stocks at elevated temperatures, however, *Hevea* is outstanding in its retention of these properties. Tensile strength dropped less than tear resistance with oven aging at 100° C, while in tests at elevated temperatures the effect was reversed. This may very well illustrate the influence of elongation on tear resistance, since in tests at elevated temperatures drop in elongation is considerably less than drop in tensile strength.

Of the four elastomers tested, *Hevea* was unique in that 72 hours' oven aging at 100° C caused a uniform drop in tensile strength and elongation. Also, when tested at 100° C, the original stock showed an increase in elongation.

### CONCLUSIONS

The fundamental fault in the stress distribution of the crescent tear-specimen has been discussed.

A new angle tear specimen has been developed, with improved stress distribution. The specimen provides greater concentration of the pulling force at the point of tearing. The need of razor nicking of the test-pieces has been eliminated, with resulting marked improvement in the uniformity of tear resistance data.

Tests carried out on four elastomers indicated that the crescent specimen values are dominated by the modulus and ultimate elongation of the material. Data obtained with the angle tear specimen indicated that tear resistance is a complex function of tensile strength and ultimate elongation.

Inasmuch as the two specimens indicate different trends in tear resistance, it is hoped that this work will stimulate further discussion among rubber technologists on the evaluation of resistance to tearing.

#### ACKNOWLEDGMENT

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## DICHLOROSTYRENES AND THEIR POLYMERS \*

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Styrene, which was first synthesized by Berthelot in 1866, has done much to foster the rapid growth of those two prodigious youngsters of chemical industry—synthetic rubber and plastics. Polymerized to polystyrene, it has made available a thermoplastic with good dimensional stability and unique insulating properties. Copolymerized with butadiene, it has made possible the widely used GR-S (or Buna-S).

Both polystyrene and GR-S have suffered from a common difficulty. They are adversely affected by heat. The strength of GR-S is greatly decreased at the high temperatures developed by heavy-duty tires<sup>1</sup>. Polystyrene wilts below the temperature of boiling water, and, as a result, its uses have been restricted.

Attempts have been made to modify polystyrene and GR-S by the addition of other compounds to the plastic or rubber-compounding formula. These have been successful in raising the heat resistance of such materials at the expense of other valuable characteristics, such as the insulating property of polystyrene.

The solution of these problems has now been accomplished by the modification of the styrene nucleus itself to dichlorostyrene. Polymerized to polydichlorostyrene, the new compound gives a plastic which combines for the first time the insulating properties of polystyrene with excellent heat resistance. Copolymerized with butadiene, it produces a rubber, recently announced, which is superior to Buna S, not only in heat resistance, but in many other important properties.

Several years ago the investigation of nuclear chlorinated styrenes began in this laboratory. It was soon found that the monomers could be polymerized readily to form stable polychlorostyrenes, and copolymerized with various other unsaturated substances to give rubberlike products.

Dichloro- styrene isomer	Refractive index $n_D^{25}$	Boiling point (°C)	Density (25/4)
2,6	1.5724	59 at 2 mm.	1.280
3,5	1.5745	53.5 at 1 mm.	1.237
2,5	1.5788	74 at 3 mm.	1.245
2,4	1.5812	69 at 2.5 mm.	1.246
2,3	1.5780	61 at 1 mm.	1.264
3,4	1.5840	76 at 3 mm.	1.243

The initial field of study was the isomers of dichlorostyrene. Nuclear substituted dichlorostyrenes were prepared from the corresponding dichlorobenzaldehydes by formation of carbinols through the Grignard reaction, followed by dehydration in the vapor phase over activated alumina. The properties given in the preceding table have been observed for the dichlorostyrene isomers.

\* Reprinted from *Chemical and Engineering News*, Vol. 22, No. 18, pages 1559-1563, September 25, 1944.

In general, these isomers have a surprisingly pleasant odor, particularly the 3,4-isomer, which has an odor resembling geraniums.

The monomeric dichlorostyrenes are very active. Highly purified samples have been observed to polymerize virtually to completion in 3 to 4 hours at 60 to 70° C. In spite of this rapid polymerization, it is possible, by working with cross-sections of less than 0.5 inch, to keep the temperature of the reaction below limits which would be injurious to the polymer. Styrene normally requires 8 to 14 hours at 130° C, after which time there is usually 1 to 3 per cent of residual monomer. The great activity of dichlorostyrene enables the polymerization reaction to go to such a degree of completion that extractable monomer residues run only about 0.1 per cent by weight.

Impurities are found to affect the polymerization reaction, usually in an adverse manner, such as catalytically breaking the chain reaction of polymerization. On the other hand, some substances are not chain breakers. For example, sulfur as  $\text{SO}_2$  introduced into the monomer in small amounts seems to aid in the growth of long chains, whereas sulfur as  $\text{H}_2\text{S}$  has the opposite effect. Figure 1 shows the effect of temperature on the average molecular weights obtained by

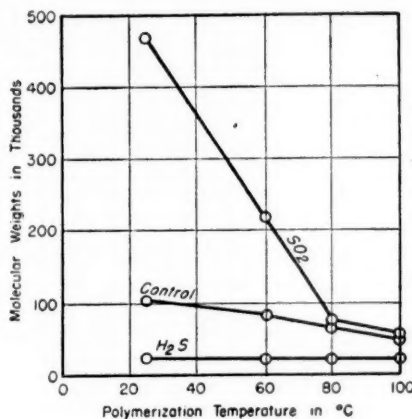


FIG. 1.—Effect of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  on molecular weight of dichlorostyrene polymer.

polymerizing the dichlorostyrene monomer alone and with small amounts of  $\text{SO}_2$  or  $\text{H}_2\text{S}$ . Polymerization occurs in spite of the presence of 0.1 per cent *p*-tertiary-butyl catechol, although at a reduced rate.

The polymers obtained from each of the isomers described above are all hard, transparent, colorless substances which resemble polystyrene in chemical resistance, solubility and general appearance<sup>2</sup>. With the exception of 3,4-dichlorostyrene, the polymers are all soluble in aromatic hydrocarbons, chlorinated solvents, some esters, and higher ketones. They are not soluble in aliphatic hydrocarbons, lower alcohols, ethers, and glycols. Some solvents, such as acetone and higher alcohols, swell but do not dissolve dichlorostyrene polymers.

The solubility of the polymer of 3,4-dichlorostyrene presents interesting possibilities. Although it is a linear polymer, it is insoluble in toluene. Only slight swelling occurs in this solvent at the boiling point. It does not dissolve in  $\text{CCl}_4$  or  $\text{CCl}_4$ -toluene mixtures, but is completely, though slowly, soluble in methyl ethyl ketone.

In addition to mass polymerization, dichlorostyrene can be polymerized in true emulsion, which gives a latexlike product before coagulation, and very finely powdered resin after coagulation.

For other purposes, the monomer may be dispersed in water, using gelatin, talc, bentonite, polyvinyl alcohol, or other conventional stabilizers, and polymerized as beads or pearls. Under proper conditions perfectly clear spheroids are obtained.

#### MATHIESON PLASTIC—A DICHLOROSTYRENE POLYMER

There are many applications for a plastic material which will maintain its shape and hardness at the boiling point of water and above. Mathieson plastic

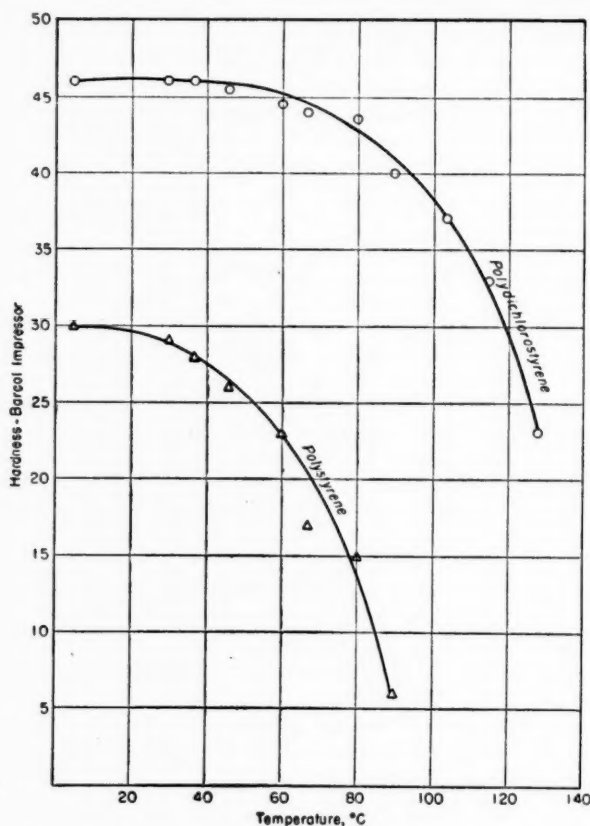


Fig. 2.—Hardness at various temperatures for injection moulded samples.

has a distortion temperature of 240° to 265° F, which is higher than that for any plastic which combines excellent electrical characteristics with good strength, machinability, and mouldability. High purity and careful control of polymerization conditions are necessary to prevent impairing the high-temperature properties of the product.

Mathieson plastic is self-extinguishing, according to ASTM D-635-41 T. When held in a flame, it undergoes pyrolysis, and the products of pyrolysis

burn. When the flame is removed, the pyrolysis stops and there is no further burning. The combustion products include  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , soot, and  $\text{HCl}$ , on account of the aromatic structure and chlorine content.

Mathieson plastic retains hardness to a remarkable degree at temperatures of  $200^\circ\text{F}$  and above. Figure 2 shows the hardness of injection-moulded samples at various temperatures. Hardness was measured by a Barcol impressor, which was applied to the samples in an oven. Comparative values for polystyrene are shown as far as readings could be made. The Rockwell hardness M-100 approaches that of thermosetting resins.

The tensile and flexural strengths of Mathieson plastic are high for a product of this type, above the range usually obtained for polystyrene. Impact strength is substantially more than polystyrene. The polymer does not become brittle at naturally occurring low temperatures.

Mathieson plastic is more compatible with conventional plasticizers than polystyrene itself. The highly plasticized polymers are particularly interesting in the composition of cements and pressure-sensitive adhesives.

Other and more detailed properties of Mathieson plastic are shown in Table I.

TABLE I  
PROPERTIES OF MATHIESON PLASTIC<sup>3</sup>

Characteristic	Mathieson Plastic	Polystyrene <sup>3</sup>	Cellulose Acetobutyrate <sup>3</sup>
Moulding qualities	Good	Excellent	Excellent
Compression moulding temp. ( $^\circ\text{F}$ )	350 to 425	275 to 375	260 to 360
Compression moulding pressure (lb./sq. in.)	2000 to 5000	1000 to 10,000	500 to 5000
Injection moulding temp. ( $^\circ\text{F}$ )	475 to 525	325 to 500	340 to 420
Injection moulding pressure (lb./sq. in.)	10,000 to 30,000	10,000 to 30,000	8000 to 30,000
Specific gravity	1.39 to 1.40	1.054 to 1.070	1.15 to 1.23
Refractive index, $n_D$	1.62 to 1.64	1.59	1.47 to 1.49
Flammability (in./min.)(ASTM-D635-41T)	Self-extinguishing	0.75 to 1.50	2.50 to self-extinguishing
Tensile strength (lb./sq. in.)	4600 to 7460	3000 to 8500	2500 to 6700
Modulus of elasticity (lb./sq. in. $\times 10^3$ )	5.0 to 7.0	1.7 to 4.7	0.6 to 2.0
Flexural strength (lb./sq. in.)	14,000 to 19,000	4800 to 19,000	2100 to 12,700
Impact strength (ft.-lbs./inch) of notch (ASTM-D256-41T)	1.0 to 1.5	0.26 to 0.4	0.5 to 7.5
Hardness (Rockwell)	>M100	M55 to M95	M23 to M72
Distortion under heat ( $^\circ\text{F}$ )	240 to 265	165 to 190	117 to 214
Dielectric strength (volts/mil)	370	500 to 700	250 to 400
Dielectric constant	2.55 to 2.65	2.5 to 2.7	3.5 to 6.4
Power factor (per cent)	<0.1	0.01 to 0.08	1.0 to 6.0
Water absorption, 24 hours (per cent)	0.02	0.04 to 0.06	1.6 to 2.1
Effect of weak acids	None	None	Slight
Effect of strong acids	None	None	Decomposes
Effect of weak alkalies	None	None	Slight
Effect of strong alkalies	None	None	Decomposes
Effect of organic solvents	Soluble in aromatic and chlorinated solvents	Soluble in aromatic and chlorinated solvents	Soluble in ketones and esters
Effect on metal inserts	Inert	Inert	Inert
Clarity	Transparent	Transparent	Transparent
Color possibilities	Unlimited	Unlimited	Unlimited

## STABILITY

The tendency to split off  $\text{HCl}$  by action of heat, light, and catalysts is negligible, probably because the chlorine in Mathieson plastic is present only as a substituent in the benzene nucleus. It is not necessary to add stabilizers to prevent demuriation, as is the case with polymers containing chlorine attached to an aliphatic structure. In spite of stabilizers, such chlorine tends to split off at the high temperatures encountered in moulding. Mathieson plastic evolves no  $\text{HCl}$  at any temperature short of actual pyrolysis, and does not need stabilizers.



## WATER ABSORPTION

Mathieson plastic absorbs less water than polystyrene under the same conditions. Even at elevated temperatures very little water is absorbed by the polymer. Figure 3 shows a comparison of water absorption by injection-

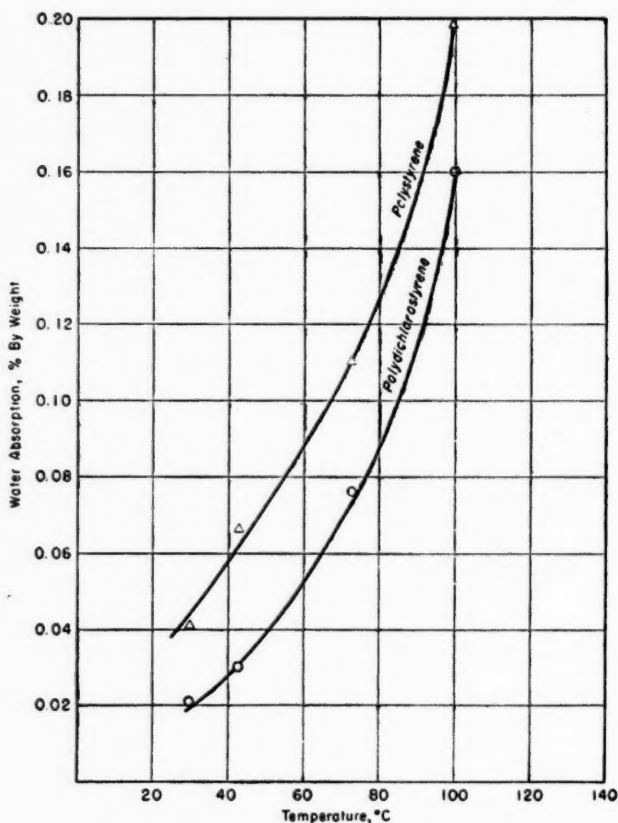


Fig. 3.—Water absorption (24-hour immersion) at various temperatures for injection-moulded samples.

moulded Mathieson plastic and injection-moulded polystyrene at various temperatures.

## CHEMICAL RESISTANCE

Mathieson plastic is unaffected by hydrochloric acid, nitric acid, sulfuric acid, ammonium hydroxide and dilute and concentrated sodium hydroxide at room temperature, when tested according to ASTM methods. When placed in sulfuric acid of 1.26 specific gravity at 90° C for 48 hours, the gain in weight was less than 0.1 per cent. There was no measurable quantity of HCl evolved during this test. Mathieson plastic is also unaffected by methanol and lower alcohols, aliphatic hydrocarbons, glycols, and vegetable oils. It is soluble in aromatic hydrocarbons, chlorinated hydrocarbons, some esters, some ethers, methylethyl ketone, and some higher ketones.

## MOULDING—GENERAL

Mathieson plastic may be moulded by conventional methods. The high distortion temperature and high melting point make some modifications necessary in injection moulding and extruding technique. The sprues, runners, and gates of the mould should be as large as consistent with the size of the cavities. Likewise, it is advisable to operate the mould at an elevated temperature of about 140° to 160° F to avoid premature setting in thin cross-sections. If this is not done, the chilled sections may interfere with the complete filling of the mould. Pieces much hotter than permissible with the usual thermoplastic can be removed from the mould and handled without danger of distortion. For some moulded shapes the moulding cycle may be longer than for polystyrene. It has been found possible to use Mathieson plastic in injection-moulding machines directly after most thermoplastics, such as nylon, polystyrene, cellulose acetate, and cellulose acetate-butyrate, without difficulty other than a moderate amount of sticking until the preceding material has been completely washed out of the machine cylinder.

Compression moulding is not generally recommended because of the extremely long cycle necessary, but where circumstances warrant, this method of moulding may be used. Mathieson plastic is readily formed into shapes by the extrusion process. Proper cooling and annealing are necessary to obtain stable pieces.

## COPOLYMERS

Dichlorostyrenes are very readily copolymerized with other unsaturated substances. This can be done either by mass or emulsion polymerization methods. The following substances are among those which have been found to form true copolymers: styrene,  $\alpha$ -methylstyrene, methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate, dimethylfuran, piperylene, quinine, 2-methylpentadiene, dimethylbutadiene, butadiene, maleic anhydride, isoprene, cyclopentadiene, indene, and chloromaleic anhydride.

## MATHIESON RUBBER—A NEW SYNTHETIC

Many of the copolymers of dichlorostyrene are rubberlike. When these are compounded in a formula of the GR-S type, they show much better oil resistance, tensile strength, elongation, tear resistance, and modulus at 300 per cent than GR-S. This is also the case for tests made at 212° F. After aging for 48 hours at 212° F, these properties are not reduced to nearly the extent that they are with GR-S. Excellent resistance to flex-cracking is shown by the Goodrich, De Mattia, and St. Joseph flexometers, and in actual road tests. Mathieson rubber not only shows these improved mechanical properties but is also easier to handle on the rubber mill than GR-S. The data on Mathieson rubber presented here compare it particularly with GR-S, but, in comparison with natural rubber also, Mathieson rubber excels in oil resistance, hot tensile strength, resistance to heat aging, and to water absorption.

## EFFECT OF DICHLOROSTYRENE CONTENT ON TREAD STOCK

The percentage of dichlorostyrene in Mathieson rubber has a controlling influence on the quality of tread stock compounded according to the formula given in Table II.

It is evident that the best performance of Mathieson rubber is found in the range of 12 to 16 per cent chlorine, equivalent to 30 to 40 per cent dichloro-

TABLE II  
COMPOUNDING AND PROPERTIES OF MATHIESON RUBBER

Mathieson rubber	100 parts by weight			
Bardol	5			
Zinc oxide	5			
W-6 Black	50			
Sulfur	2			
Mercaptobenzothiazole	1.5			
Curing temperature	280° F			
Chlorine in crude rubber (%)	8.8	12.5	16.2	23.2
Curing time (minutes)	70	70	70	80
Tensile strength (lbs. per sq. in.)	2530	3490	3960	2400
Elongation (%)	490	735	745	560
Modulus at 300% elongation	1230	690	840	..
Durometer hardness (Shore)	65	61	60	73
Set (%)	13	28	31	38

styrene. More evidence on the superior heat resistance of Mathieson rubber was obtained in the region of lower chlorine, as is shown in Figures 9 and 10.

#### LOW-TEMPERATURE PROPERTIES

The low-temperature flexibility of Mathieson rubber tread stocks compounded from the formula in Table II is more satisfactory at the lower end of the range of 12 to 16 per cent chlorine. Mathieson rubber with 14 per cent chlorine (based on the crude rubber) was slightly hard at  $-50^{\circ}\text{C}$ , and broke at  $-65^{\circ}\text{C}$ . By comparison, smoked sheet compounded by the same formula was hard at  $-50^{\circ}\text{C}$ , and did not break at  $-60^{\circ}\text{C}$ .

#### COMPOUNDING MATHIESON RUBBER

The milling characteristics of Mathieson rubber are excellent. For example, in one large batch the crude rubber broke down in 2 minutes sufficiently to begin adding the black, and was as soft as GR-S is after 5 minutes. In the break-down on the rolls, Mathieson rubber handled very much like smoked sheet. When the compounding formula for GR-S issued by the Office of the

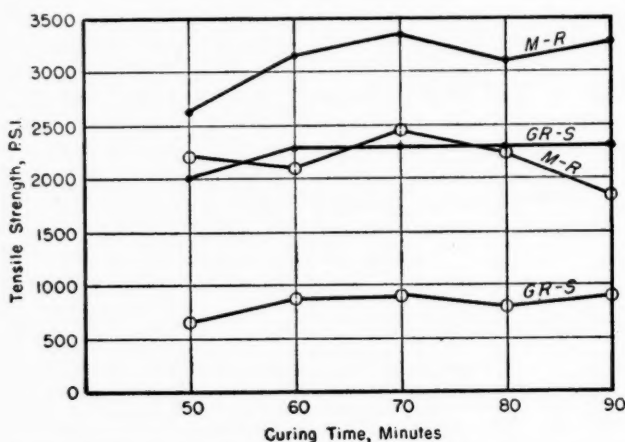


Fig. 4.—Tensile strength of unaged Mathieson rubber (18.7% chlorine). Solid circles represent values obtained when samples tested at room temperature, the open circles when tested at  $212^{\circ}\text{F}$ .

Rubber Director, and given above, was used, the break-down was 2 to 3 minutes. Accelerator was added at the end of 4 minutes, black at 11, softener at 14, zinc oxide at 15, and sulfur at 16. The stock was cut off the roll at 18, and then refined for 3 minutes. The temperature of the stock was about 120° F.

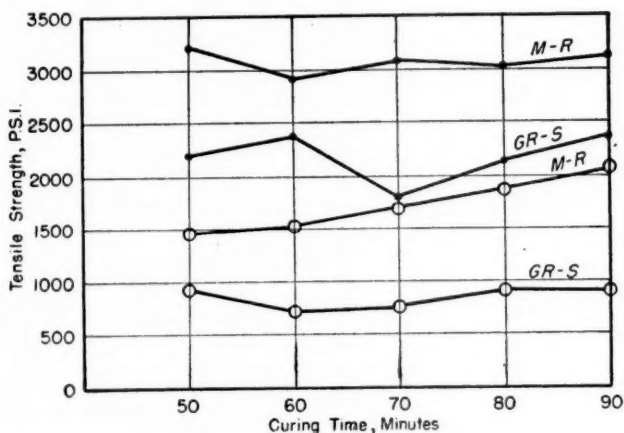


Fig. 5.—Tensile strength of Mathieson rubber (18.7% chlorine). Aged 24 hours at 212° F. Solid circles represent tests made at room temperature, open circles at 212° F.

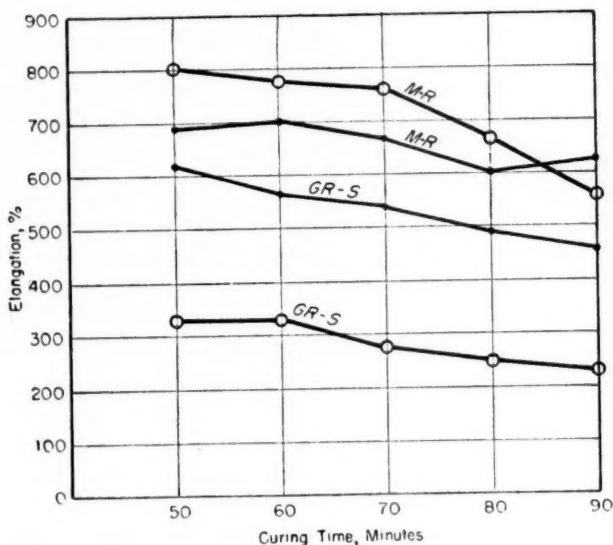


Fig. 6.—Elongation of unaged Mathieson rubber (18.7% chlorine). Solid circle represents test at room temperature, open circle at 212° F.

Figures 4 to 8, inclusive, show the behavior of Mathieson rubber containing 18.7 per cent chlorine when compounded by the GR-S standard formula and cured at 280° F. Figure 4 shows a tensile strength for Mathieson rubber of 3,300 lbs. per sq. in, compared with a value for GR-S of 2,300 lbs. per sq. in,

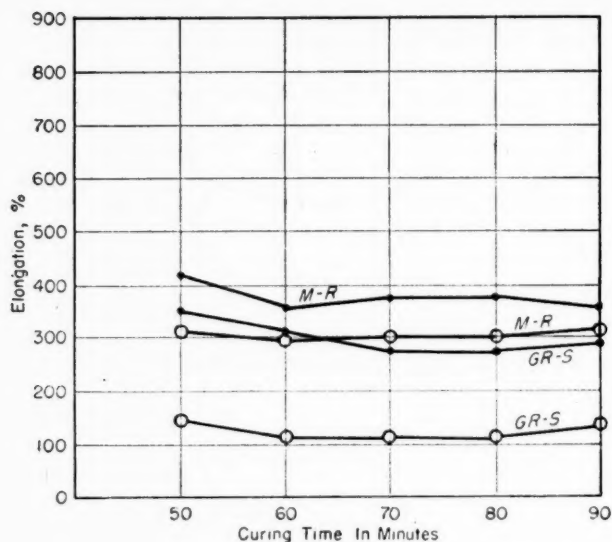


Fig. 7.—Elongation of Mathieson rubber (18.7% chlorine) aged 24 hours at 212° F. Solid circles represent tests at room temperature, open circles at 212° F.

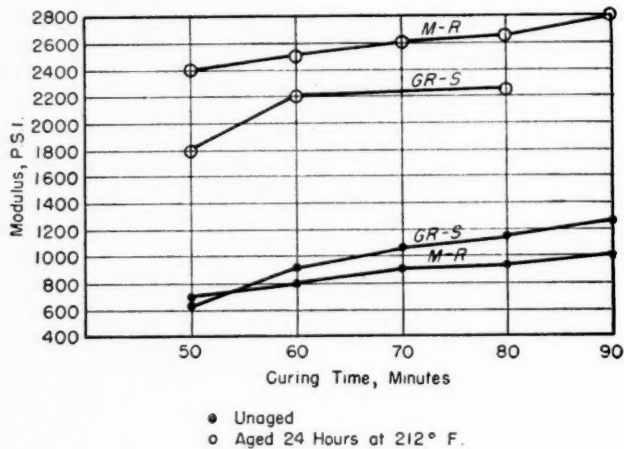


Fig. 8.—Modulus at 300% elongation of Mathieson rubber (18.7% chlorine).

A similar advantage is shown for samples tested at 212° F. After aging for 24 hours at 212° F, the situation is similar (Figure 5). The same general results are found in Figures 6, 7, and 8, which give the corresponding elongations and moduli at 300 per cent.

Figures 9 and 10 compare the tensile strengths and elongations of a sample of Mathieson rubber containing 12.9 per cent chlorine and of GR-S compounded by the formula given below in Table III. The curing temperature used was 287° F, and no stearic acid was used with GR-S. The tensile strength of this

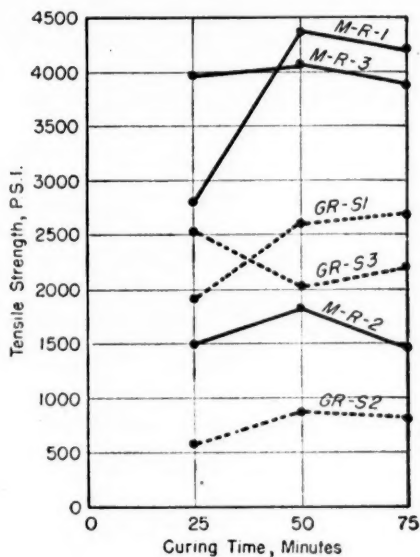


Fig. 9.—Tensile strength of Mathieson rubber (12.9% chlorine). Data are from tests made at room temperature, and the curves numbered 1 represent unaged samples, 2 represent the samples tested at 212° F, and 3 represent samples aged for 48 hours at 212° F.

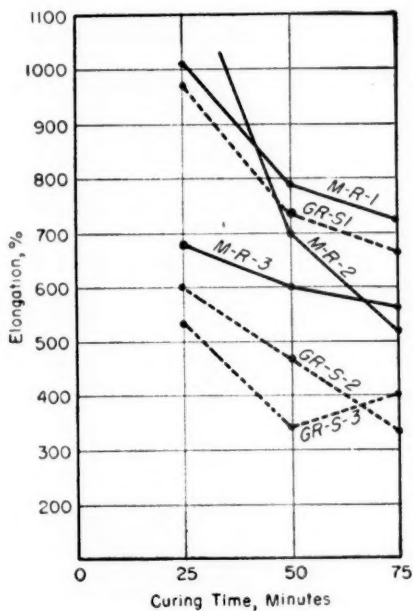


Fig. 10.—Elongation of Mathieson rubber (12.9% chlorine). In this figure, curves 1, 2, and 3 have the same description as in Figure 9.

TABLE III  
COMPOUNDING FORMULA

Rubber	100 parts by weight
Channel Black (E.P.C.)	45
Zinc oxide	5
Sulfur	1.7
Santocure	1.2
Stearic acid	2.5
B.L.E.	2.0
Pine tar	2.5
Bardol	2.5

rubber was 4,350 lbs. per sq. in. tested at room temperature and 4,000 lbs. per sq. in. after ageing 48 hours at 212° F. The hardness of compounded Mathieson rubber containing 18.7 per cent chlorine was 88 (Table IV) after aging.

TABLE IV  
SHORE HARDNESS OF MATHIESON RUBBER COMPOUNDED BY GR-S FORMULA.  
CHLORINE IN MATHIESON RUBBER 18.7 PER CENT; TESTED  
AT ROOM TEMPERATURE

Curing Time (Minutes)	Unaged		Aged 24 Hours at 212° F	
	Mathieson rubber	GR-S	Mathieson rubber	GR-S
50	64	57	84	69
60	64	59	87	70
70	66	60	88	72
80	68	61	88	73
90	69	61	88	73

A more desirable hardness of 70 was obtained after aging the product containing 12.9 per cent chlorine.

The ability of Mathieson Rubber to withstand tearing is outstanding compared with GR-S, as shown in Table V.

TABLE V  
WINKLEMAN TEAR TEST ON MATHIESON RUBBER COMPOUNDED BY GR-FORMULA  
CHLORINE IN MATHIESON RUBBER 18.7 PER CENT; CURING  
TEMPERATURE 280° F

Curing Time, Minutes	Unaged				Aged 24 Hours at 212° F			
	Tested at room temp.		Test at 212° F		Tested at room temp.		Test at 212° F	
	Mathie- son rubber	GR-S	Mathie- son rubber	GR-S	Mathie- son rubber	GR-S	Mathie- son rubber	GR-S
50	315	175	265	120	215	165	255	210
60	330	275	240	175	245	175	280	235
70	300	230	220	185	320	195	270	195
80	310	245	250	170	310	165	270	215
90	265	230	265	185	255	140	270	160

Mathieson rubber, compounded essentially as shown in Table III, was examined on the St. Joseph, Goodrich, and DeMattia flexometers. The resistance to flex-cracking was excellent. GR-S failed at 54,000 flexings unaged, and 26,000 aged, on the DeMattia, while Mathieson rubber was still flexing at 100,000. In heat build-up tests involving 30 minutes of flexing, the temperature of the GR-S sample rose to 324° F when the test piece blew out, while Mathieson rubber heated only 228° F, and was undamaged.



## TRUCK-TIRE TESTS

While GR-S performs satisfactorily in passenger car tires driven at 35 miles per hour or less, it is not acceptable for commercial tires in which the generation of heat is more extensive<sup>1</sup>. GR-S tires do not stand overloading or high speeds. There is, therefore, a definite need for a new synthetic rubber which withstands overloading and high-speed operation. In actual tests, Mathieson rubber promises to meet this need.

Early in 1944 a tread test was run with Mathieson rubber treads on  $9.00 \times 20$  tires, S-5 construction. This test, requested by the Office of the Rubber Director, was made at San Antonio, Tex., by the ORD group. The results were favorable. Mathieson rubber tires with natural rubber carcasses withstood the road conditions, speed, and heavy loading very acceptably, as shown by the fewer and smaller cracks which formed in the Mathieson rubber tires.

Because this test was run during cold weather, the Office of the Rubber Director requested that another be made during the summer, when a greater difference should be shown in heat resistance between Mathieson rubber and GR-S. Such tests were run and, though data on the results are not yet available, preliminary reports indicate that the tires showed up well.

## ANALYTICAL VALUES ON CRUDE MATHIESON RUBBER

The following analytical values were shown for two batches of Mathieson rubber crude sheet:

TABLE VI

Chlorine (Parr bomb) (%)	12.9	18.7
Dichlorostyrene (%)	31.5	45.6
Iodine value (Wijs)	277	217
Toluene solubility by Soxhlet extraction (%)	90	79.4
Molecular weight on soluble portion (Ostwald viscosimeter)	190,000	148,000

## PERMEABILITY TOWARD GASES

The specific permeability of three different preparations of Mathieson rubber crude sheet to hydrogen, helium, and carbon dioxide is given in Table VII in cc. per cm. per sq. cm. per minute times  $10^6$ .

TABLE VII

Chlorine content of Mathieson rubber (%)	15.5	20	30
Specific permeability			
Hydrogen	9.2	6.2	1.9
Helium	6.1	5.0	2.1
Carbon dioxide	18.7	7.4	..

The low permeability values make this material interesting as a possible coating for balloon cloth.

## ELECTRICAL PROPERTIES

The specific inductive capacity was 5.0 and the power factor 4.5 at 1,000 cycles per second on a sheet of compounded Mathieson rubber  $6 \times 6 \times 0.070$  inches. The compound contained clay, zinc oxide, EP channel black, paraffin, stearic acid, antioxidant, sulfur, and accelerator.

## MOISTURE ABSORPTION

Crude sheets of Mathieson rubber  $5 \times 2.5 \times 0.08$  inches were cut out and weighed. They were immersed in water at  $70^\circ \text{C}$  for 20 hours, removed, dried

with a towel, and reweighed. The gain in weight is given in mg. per sq. in. of surface, neglecting the edges (see Table VIII).

TABLE VIII

Sample	Absorption
Mathieson rubber	2.2
GR-S	25
Smoked sheet	18
Special crepe	3
Hycar-OR	33

## OIL RESISTANCE

Figure 11 shows the effect of soaking samples of Mathieson rubber, GR-S, and natural rubber tire stocks at 55° C in light Circo oil, a light processing oil

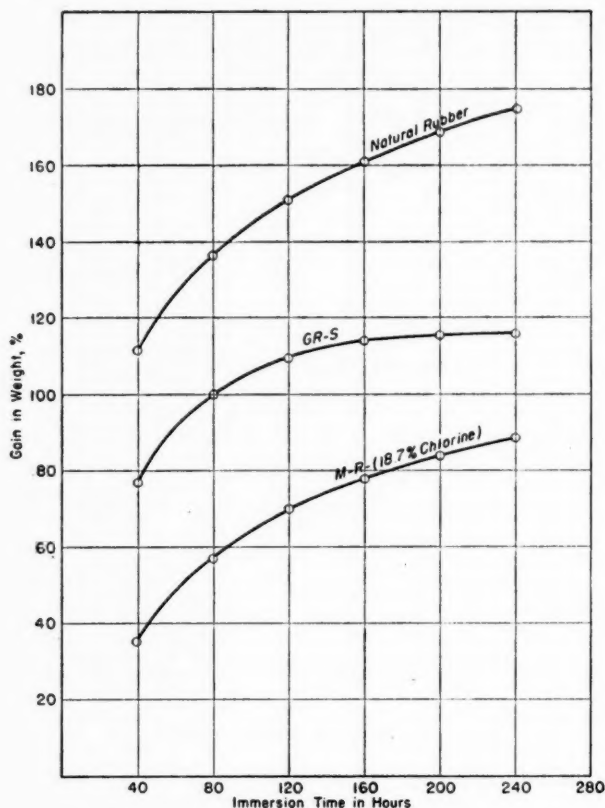


Fig. 11.—Weight gain of tire stocks immersed in light Circo oil at 55° C.

used for softening and plasticizing rubber. While the oil resistance of Mathieson rubber is not so good as that of Neoprene, Hycar-OR, or Thiokol, it is better than that of either GR-S or natural rubber.

## OTHER PROPERTIES AND USES

Mathieson rubber also finds application in hard-rubber compositions which are tough, dense, hard, and resistant to aqueous alkalies and acids at moderate temperatures. Hardness can be controlled, not only by the percentage of sulfur, as is done in the case of hard rubber made from natural rubber, but also by varying the content of the dichlorostyrene in the crude Mathieson rubber.

Mathieson rubber shows promise in a variety of adhesive compositions.

## ACKNOWLEDGMENT

The information given above is the result of coöperative efforts of members of the staff of The Mathieson Alkali Works (Inc.) together with General Tire and Rubber Co., Whyte Manufacturing Co., Phelps-Dodge Copper Products Corp. and the National Bureau of Standards.

## REFERENCES

<sup>1</sup> *Automotive & Aviation Ind.* **89**, 26, 66 (1943).

<sup>2</sup> Trichlorostyrenes, prepared properly by dehydrogenation of chloroethyltrichlorobenzenes, are also surprisingly active monomers, with boiling points of 82–84° C (2 mm.), and with  $n_D^{25}$  1.5943. They polymerize very readily to resins, which have ASTM distortion temperatures of 120° C or higher, and they copolymerize to rubberlike products.

<sup>3</sup> From "Technical Data on Plastic Materials", by Plastic Materials Manufacturers' Association.

# ANTIOXIDANT INFLUENCE OF SULFUR IN MASTICATION OF RUBBER \*

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS

WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

## INTRODUCTION

The nature of the oxidation processes in unvulcanized rubber is by no means well understood. It seems clear, however, that the oxidation of raw rubber differs in some fundamental manner from the oxidation of vulcanized rubber, and Dawson<sup>1</sup> has briefly drawn attention to some of the phenomena which suggest this difference.

The development of surface tackiness under the influence of light, and the increase of plasticity during mastication, are both believed to be due to oxidation of the unvulcanized rubber, and these effects may be used to provide some indication of the degree of oxidation which has occurred.

Blake and Bruce<sup>2</sup> found that the production of tackiness in raw rubber due to light was increased by the introduction of antioxidants suitable for vulcanized rubber; i.e., the substances which act as antioxidants towards vulcanized rubber may be oxidation catalysts for raw rubber. On the other hand, there are many substances which will diminish the influence of light in developing tackiness in raw rubber, and will also inhibit the catalytic oxidation by the ordinary "antioxidants."

Chief among these materials which are negative catalysts for the oxidation of raw rubber is sulfur. Thus, Blake and Bruce<sup>2</sup> found that 0.1 per cent of sulfur reduced the rate of tack-formation at least 60-fold, the experiment not being continued until the standard degree of tackiness was produced. Sulfur also inhibits the oxidation of other autoxidizable substances; Moureu and Dufraisse<sup>3</sup> found that 0.1 per cent of sulfur prevents the autoxidation of benzaldehyde, and sulfur produces also a marked depression of the autoxidation of paraffins at 160° C<sup>4</sup>. Although sulfur retards the polymerization of styrene<sup>5</sup>, which is catalyzed by oxygen, it has no effect on the oxidation of styrene in the cold<sup>6</sup>. Scott<sup>7</sup> found that the rapid oxidation of raw rubber caused by incorporation of Prussian blue could be inhibited by adding small amounts of sulfur.

On the other hand, work on vulcanized rubber does not lead to the same conclusions. Yamazaki and Okuyama<sup>8</sup> found that there was no correlation between the amount of free sulfur and the aging properties, and Dufraisse and Drisch<sup>6</sup> concluded that sulfur has no antioxygenic effect on vulcanized rubber. Dufraisse and Etienne<sup>9</sup>, however, found that the oxidizability of the vulcanizates passes through a minimum at a small concentration of free sulfur, the actual amount being of the order of 1-3 per cent and dependent on the type of compound.

In connection with the oxidation associated with changes in plasticity, Blake and Bruce<sup>2</sup> drew attention to the possible existence of a parallelism between activation of the development of tackiness and increase of plasticity on milling. They conducted some milling experiments, using two activators and three inhibitors of tackiness, and concluded that "there seems to be no

\* Reprinted from the *Journal of Rubber Research*, Vol. 13, No. 12, pages 166-167, December 1944.

entirely satisfactory correlation between the production of tackiness by the various reagents and their effect on plasticity". Blake and Bruce did not, however, include sulfur among the antioxygens in their milling experiments, and the experiments described in this report were undertaken to complete the data in this respect.

In these experiments, two batches of raw rubber were masticated under comparable conditions, but in one case sulfur was added at the beginning and in the other, only at the end of the process. If sulfur possesses an antioxygenic effect in respect to mastication oxidation also, the plasticity of the former stock should be less than that of the latter. If a marked effect of this kind were found, it would have an important bearing on mixing technique, because addition of the sulfur at the beginning would reduce the efficiency of subsequent milling.

#### PREPARATION OF THE SAMPLES AND DETAILS OF TEST METHOD

The mixings contained 1000 grams of smoked sheet and 50 grams of sulfur; in the case of mixing A, the sulfur was added at the beginning; in the case of mixing B, the sulfur was incorporated after the rubber had been masticated. The mill nip and roll temperature were kept constant ( $52^{\circ}\text{C}$ ) for the two mixings, the period of mixing being 30 minutes in each case. The rolls used were  $6 \times 12$  in., revolving at 20 and 30 r.p.m., respectively.

Short cylinders of rubber  $1.4 \times 1.4$  cm. were cut from the stock, the weight being adjusted until a volume of exactly 2 cc. was obtained. The samples were preheated for 15 minutes at  $90^{\circ}\text{C}$ , and then maintained at this temperature while being compressed between parallel plates under a load of 5 kilograms. The thickness of the samples was measured after various periods of compression, and the mean values from three samples of each of the mixings are given in Table 1.

TABLE 1  
PLASTICITY RESULTS. AVERAGE THICKNESS OF  
SAMPLES AFTER COMPRESSION FOR  
VARIOUS PERIODS OF TIME

Period of compression (min.)	Mixing A (mm/100)	Mixing B (mm/100)
0.25	321	326
0.50	264	274
0.75	236	243
1	217	224
1.5	188	196
2	170	177
3	144	153
4	128	134
5	117	123
6	108	114
7	101	106
8	94	100
9	89	94
10	85	89

The tendency of the stocks to exhibit elastic recovery after compression was also measured. Test pieces  $11 \times 11$  mm. and 8 mm. thick were compressed between sheets of cellophane after 15 minutes of preheating at  $90^{\circ}\text{C}$ . The thickness was reduced from 8 to 1.6 mm. in 5 seconds, and was maintained at the reduced value for a further 5 seconds. The pressure was then quickly released and the thickness again measured after keeping the specimen for 5

min. at 90° C, and allowing to cool. The results are given in Table 2, the figures being the final increase in thickness expressed as a percentage of the reduced thickness (1.6 mm.); the mean of three values are given; the average range of the three values was 4.4 units on the percentage scale.

#### EXPERIMENTAL RESULTS

At every period of compression the average thickness of the samples from mixing B is somewhat greater than that from mixing A, which suggests that mixing A is the softer, even though the sulfur was added at the beginning; *i.e.*, if anything, the sulfur has increased the oxidation instead of retarding it. The extent of the variation among the results for the three samples from each mixing suggests that the difference between the mean results may be real; as the difference is only small, it may be due to slight differences between two batches of the raw rubber.

These figures for recovery after compression also suggest that mixing A is the more plastic and hence more oxidized, even though the sulfur was incorporated at the beginning. The variation among the results from the three individual samples of each rubber is so large, however, that the difference between the mean values given in Table 2 cannot be regarded as demonstrating a significant difference.

TABLE 2  
RECOVERY AFTER COMPRESSION

Mixing	Final increase in thickness expressed as a percentage of the reduced thickness
A	16.0
B	18.3

#### CONCLUSIONS

The results for plasticity and recovery obtained in this work do not support the view that sulfur is a negative catalyst for the oxidation which is the essential factor in mastication on the mixing mill. The slightly higher plasticity of the mixing to which sulfur was added at the beginning suggests, on the contrary, that greater oxidation occurred while the sulfur was present. These results support the conclusion of Blake and Bruce that no satisfactory correlation exists between the effects of sulfur on the production of tackiness due to light and on the rate of mastication. This result is surprising, in view of the findings of Scott that the addition of sulfur decreased the plasticity of mixings containing Prussian blue, even though no vulcanization had occurred. As, however, in the latter tests, the stocks were overmilled, it may be that in the present experiments, where milling was carried out for a normal period and at a relatively low temperature, the sulfur did not have time to dissolve in the rubber and so become effective. Moreover the mechanism of oxidation catalyzed by Prussian blue may differ from that occurring in the absence of a catalyst.

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## MASTICATION AND RATE OF SET-UP. PART II \*

S. BUCHAN

In the earlier communication<sup>1</sup> it was shown that the length of time of milling of a mixed rubber exerted a marked effect on the rate at which it commenced to scorch. The longer the time of milling, the slower was found to be its rate of set-up. It is intended in this paper to give a brief account of some experiments which were undertaken with a view to deciding which factor or factors in the process of mastication are responsible for this retardation of the initial stages of vulcanization.

During the milling of rubber only a limited number of factors can be considered as having any effect on its subsequent behavior as far as its rate of set-up is concerned. These are, decomposition of the accelerating components due to heat and pressure, softening of the rubber due to mechanical working, disaggregation or other causes, breakdown of the ultimate rubber particles, depolymerization, or, finally progressive oxidation of the rubber throughout the milling and mixing process.

The possibility of decomposition of the accelerator during milling was examined by adding the accelerator to one batch at the beginning of the mixing process, adding it to another at the end and comparing the results of the rates of set-up on the two rubbers. Softening of the rubber without resorting to mechanical means was carried out by adding various softeners to the rubber while in solution and dispersing these by gentle stirring. It is of interest to note that the addition of softeners to the mixing without simultaneous mechanical working resulted in only a slight lowering of the plasticity reading (Y value), which seems to indicate that, for the effective development of softening action, mechanical working or the catalytic effects induced during mechanical working are essential.

On the assumption of Hauser's view of the constitution of the rubber particle that it exists in latex essentially as a tough outer skin of  $\beta$ -rubber enclosing a viscous inner phase of  $\alpha$ -rubber, it would appear to be reasonable to expect prolonged milling, coupled with the heat and pressure caused thereby, to result in the rupturing of progressively more and more of these ultimate rubber units and the release of correspondingly increasing amounts of  $\alpha$ -rubber<sup>2</sup>. On this view of the mechanism of mastication the possibility exists that retardation of the rate of set-up is due to the liberation in active form of the viscous  $\alpha$ -rubber.

The effect of heat-depolymerization on the rate of set-up was studied concurrently with the effect of oxidation. The action of oxygen on rubber and its effect on the rate of scorching was examined from two angles, first, oxidation by the absorption of oxygen of molecular dimensions and, second, oxidation by the gas in its reactive atomic condition.

Oxidation during the process of mastication has been the subject of several investigations, and from these two main theories have been evolved: that oxidation occurs because of catalytic action developed by the rubber during milling

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and, secondly, that it occurs by the decomposition of primarily formed unstable peroxides. Results given later on the molecular oxidation of rubber seem to show that formation of unstable peroxides with subsequent evolution of atomic oxygen does not occur, although a large excess of oxygen may be absorbed by the rubber at high temperatures. If this is so, it follows that the primary formation of peroxides in masticated rubber must also be a catalyzed reaction, so that in both theories catalytic activation of the oxygen appears to be necessary.

In carrying out experiments the base mixing employed, unless otherwise specified, was:

Smoked sheet rubber	100
Zinc oxide	4
Sulfur	3
Stearic acid	2
Mercaptobenzothiazole	2

The rate of set-up was determined in all cases at 120° C by immersing 2-cc. samples in glycerol at that temperature, removing them after fixed times of heating, water-cooling, and testing their plasticities by a Williams type of plastometer.

#### DECOMPOSITION OF THE ACCELERATING COMPONENTS DURING MILLING

To test whether retardation in the rate of set-up was caused by the accelerator undergoing gradual decomposition on milling, two batches were mixed so as to give, approximately, the same plasticity readings. In mixing the first batch the raw rubber was milled for a long period before addition of the curing ingredients, whereas in the second batch the ingredients were added early in the process, and the mixed rubber was masticated until it reached approximately the same degree of plasticity as the first.

TABLE 1

	RAW RUBBER MASTICATED					
Time (min.)	0	4	6	8	10	12
Plasticity (Y)	1.23	1.27	1.30	1.60	3.30	6.00
	MIXED RUBBER MASTICATED					
Time (min.)	0	4	6	8	10	12
Plasticity (Y)	1.10	1.10	1.10	2.40	4.75	5.60

Of the two batches, the second one, in which the accelerating and curing ingredients were subjected to prolonged working on the mill, shows, if anything, the greater speed of set-up, indicating that accelerator break-down does not account for the retardation caused by excessive mastication.

#### THE EFFECT OF SOFTENERS ON THE RATE OF SET-UP

Owing to the pronounced effect of mastication on the rate of set-up of a mixing, the addition of softeners was not carried out on a mill, where slight variations caused by the presence of a softener might well be masked by variations in the mixing procedure.

The softeners examined were dissolved or dispersed in solvent naphtha (95 per cent of which distilled under 80° C), and added to a mixed rubber of the following composition:

Smoked sheet rubber	100
Zinc oxide	4
Sulfur	3
Stearic acid	0.25
Mercaptobenzothiazole	2

The mixtures were allowed to soak for 48 hours, stirred occasionally so that homogeneous solutions were ultimately obtained, poured on to a clean zinc tray, and allowed to evaporate to dryness at a temperature of from 70° to 80° F. The rubber residues were then sheeted to the required thickness and enclosed air or solvent expelled by passing, alternately with the control, between mill rolls maintained at fairly high temperatures (160° to 170° F). The rubber sheets obtained in this way were rested for 24 hours, samples cut out and the rates of set-up determined. (Table 2.)

TABLE 2

Softener	Percentage on rubber 100	Plasticity (min.)					
		0	4	6	8	10	12
Control (1)	Nil	2.29	2.32	2.75	3.53	4.87	—
Paraffin oil	2	2.25	2.20	2.52	3.41	4.98	—
Paraffin oil	4	2.20	2.20	2.50	3.38	5.69	—
Paraffin oil	6	2.10	2.22	2.30	3.00	4.77	—
Prices rubber oil	2	2.28	2.25	2.60	3.24	4.92	—
Prices rubber oil	4	2.22	2.22	2.28	3.30	4.78	—
Prices rubber oil	6	2.13	2.19	2.40	3.18	4.81	—
Zinc stearate	2	2.42	2.45	2.52	3.80	5.59	—
Control (2)	Nil	2.26	2.25	2.30	3.05	4.55	—
Petrolatum	2	2.20	2.20	2.40	3.20	4.80	—
Petrolatum	4	2.19	2.10	2.28	3.32	4.80	—
Petrolatum	6	2.08	2.07	2.30	3.30	4.52	—
Paraffin wax	2	2.20	2.10	2.20	2.80	3.22	4.30
Paraffin wax	4	2.10	2.00	2.20	2.80	3.20	4.10
Pine tar oil	2	2.20	2.25	2.30	3.10	4.75	—
Pine tar oil	4	2.20	2.10	2.20	2.40	4.60	—
Pine tar oil	6	2.10	2.20	2.10	2.20	2.75	4.50
Stearic acid	2	2.10	2.01	2.18	2.70	4.10	—
Coumarone-indene resin	2	2.14	2.10	2.18	2.80	4.10	—

When the results shown in Table 2 are analyzed, it becomes clear that most inert softeners, such as paraffin, rubber oil, zinc stearate and petrolatum, have little or no effect on rate of set-up, although an exception does occur in the case of paraffin wax, which exhibits retarding properties to a surprisingly large degree. Acid or acid-containing softeners such as stearic acid, coumarone-indene resin and pine tar oil, on the other hand, all function as retardants, probably because of interaction between their acidic components and the accelerator. The retarding effects of stearic acid and of pine tar on the rate of set-up were also noted by Thies<sup>3</sup>.

#### BREAKDOWN OF THE RUBBER PARTICLE

The simplest method by which the  $\alpha$ -rubber phase, if still present as such in the mixed rubber, could be released without milling seemed to be by swelling and rupturing the outer skin of  $\beta$ -rubber by means of a rubber solvent. By this means the solution of rubber on drying off should yield a heterogeneous mixture of free  $\alpha$  and  $\beta$ -rubbers, slower in its rate of set-up than the original rubber. The rubber mixture shown below was tested for its rate of set-up, let down in solvent, and shaken until a homogeneous solution was obtained. The solution was dried at a temperature of 70° to 80° F, the residual rubber

sheeted on warm rolls to a suitable thickness, and its rate of set-up again determined.

Smoked sheet rubber	100
Zinc oxide	4
Stearic acid	2
Tetramethylthiuram disulfide	3

TABLE 3

	Plasticity (min.)						
	0	4	8	12	16	24	32
Original rubber	1.55	1.40	1.60	1.85	2.40	3.25	4.60
Rubber from solution	1.50	1.50	1.60	1.70	2.30	3.30	4.30

The results shown in Table 3 indicate that breakdown of the rubber globule, if still present as such in sheeted rubber, does not account for variations in the rate of set-up caused by mastication.

### OXIDATION OF RUBBER

Oxidation was effected in several ways, both by the use of oxygen in molecular condition and by its use in the active atomic form.

(1) *Molecular oxygen in the cold.*—A solution consisting of the standard rubber mixture in naphtha was oxidized by bubbling through it a stream of oxygen from a cylinder for a period of 72 hours. At intervals of 24 hours part of the oxidized solution was removed, the solvent allowed to dry off at 70° to 80° F, and the rate of set-up of the residual rubber determined as described previously.

TABLE 4

Time of oxidation	Plasticity (min.)				
	0	2	4	6	8
Control	2.20	2.26	2.55	3.85	6.62
24 hours	1.98	2.02	2.80	3.95	6.57
48 hours	2.25	2.28	2.65	3.75	6.30
72 hours	2.10	2.20	2.40	3.60	6.05

It will be observed from Table 4 that oxidation in the cold with oxygen at atmospheric pressure has no appreciable effect on the behavior of the rubber.

(2) *Molecular oxygen (air) under pressure at a high temperature.*—The method employed was similar to that used by Ungar and Schidrowitz for the preparation of softened rubber. Smoked sheet, cut into small pieces roughly one square inch in area and one eighth of an inch thick, was loaded on a gauze tray and placed in a steam jacketed air oven, the inside cavity of which could be filled with air under pressure. Batches of rubber cut up as described were oxidized in this oven for periods of 2, 4, 6, and 8 hours at a temperature of 287° F, and under an air pressure of 40 lbs. per sq. in. Batches of the standard rubber quality were then mixed, using these oxidized rubbers, each batch being processed to the same specification and under as nearly the same conditions as possible. Mixings were carried out in duplicate and rate of set-up measurements made on each, the results quoted below being average figures.

TABLE 5

Time of oxidation of raw rubbers	Plasticity (min.)				
	0	2	4	6	8
Control	2.90	3.00	3.59	6.26	—
2 hours	1.95	2.22	3.98	6.08	—
4 hours	1.96	2.51	4.85	6.97	—
6 hours	1.33	1.30	3.14	5.32	6.40
8 hours	0.92	1.03	2.79	4.79	6.02

From Table 5 it will be seen that oxidation after 6 and 8 hours under the conditions mentioned does give retardation of the rate of set-up, but that this retardation is only slight when compared with that obtained when the control sample is softened by mill mastication to give plasticities of the same order as those obtained by oven-oxidation (Table 6).

Rubbers oxidized in the air-oven for 2 and 4 hours, respectively, do not appear to line up with those oxidized for 6 and 8 hours, respectively, relative to the control sample. Their positions, however, may be explained as follows. When the control rubber and the rubbers oxidized for 2 and 4 hours are compounded with their curing ingredients on the mixing mill, the retardation of the rate of set-up caused by the milling of the hard control rubber is found to be actually greater than the combined retardations on the oxidized rubbers caused by oven-oxidation plus milling. The comparative softness of the oxidized rubbers tends, apparently, to minimize very considerably the effect which is produced by the mill on a harder rubber.

TABLE 6

	Plasticity (min.)						
	0	2	4	6	8	10	12
Control	2.90	3.00	3.59	6.26	—	—	—
A	2.00	1.98	3.00	4.10	6.10	—	—
B	1.30	1.35	1.47	2.74	5.61	—	—
C	0.98	1.00	1.00	1.70	4.05	6.50	—

In these experiments, therefore, on the oxidation of rubber with oxygen of molecular proportions it is fairly obvious that the results do not line up with those obtained on the mixing mill. The figures obtained on the more highly oxidized rubbers do show a slight tendency towards retardation of their rates of set-up, and it may be that if it were possible in oven-oxidized rubber to duplicate the conditions of strain under which rubber exists during mastication, a better correlation would be obtained between initial plasticity readings and rates of set-up, using mill-masticated rubber as a standard.

(3) *Atomic oxidation with free oxygen in the cold.*—Oxidation of the mixed rubber was effected in this experiment by allowing hydrogen peroxide to act over a period of 120 hours on a solution of the rubber at a temperature of 38° C. The hydrogen peroxide used was of 10-volume strength, 25 cc. being used to each 222 grams of mixed rubber. 25 cc. of water were added to a similar weight of the control rubber, also in solution. After the specified time had elapsed, the solutions were dried in air at 70° to 80° F, the residual rubbers sheeted on warm mill-rolls and their rates of set-up determined.

TABLE 7

Batches	Plasticity (min.)								
	0	4	8	12	16	28	36	44	52
Control	1.80	1.95	2.20	2.80	4.30	—	—	—	—
A	1.70	—	1.65	—	1.70	1.70	2.20	3.10	4.00
B	1.70	—	1.60	—	1.50	1.60	3.00	3.60	4.95
C	1.60	—	1.60	—	1.50	1.50	2.50	3.50	4.20
D	1.60	—	1.50	—	1.60	1.75	2.20	3.80	4.30

When the results shown in Table 7 for the rate of set-up are compared with those obtained by over-milling without the addition of an oxidizing agent (Table 6), it will be noted that considerable retardation of the rate at which

set-up proceeds occurs in both experiments, but it is much more marked in the case of the peroxide-treated rubber. Oxidation with atomic oxygen retards the rate of set-up markedly while affecting only slightly the actual plasticity of the rubber; molecular oxidation, coupled with depolymerization, on the other hand, reduces the plasticity reading of the rubber considerably, but has little effect on the initial stages of vulcanization.

(4) *Oxidation in the presence of a catalyst.*—The experiments under this heading were carried out to see whether it is possible to convert molecular oxidation into atomic oxidation by means of a catalyst mixed into the rubber, the degree of retardation of the rate of set-up to be regarded as a measure of the amount of atomic oxidation taking place. It was thought that in this way it would be possible to duplicate with more accuracy the stages through which rubber passes while being depolymerized and oxidized during mastication. The catalyst employed was precipitated copper powder. A considerable difference of opinion existed, and probably still exists, as to whether copper in the presence of rubber acts as an accelerator of depolymerization or of oxidation. If it functions as the former, its action would become evident by a greater degree of depolymerization as measured by plasticity, but if the latter its presence would be shown by a decrease in the rate of set-up of a mixing made from the rubber.

In the first experiment five batches of raw rubber were masticated gently on warm rolls, and small quantities of precipitated copper powder were incorporated into four of them. Each batch of rubber was processed as nearly as possible under the same conditions and cut off the rolls at the end of a fixed period. The five batches were placed in an air oven at 70° C, and allowed to remain there in the dark for 88 hours, after which curing ingredients were added to each on the mixing mill, and their rates of set-up determined.

TABLE 8

Rubber	Plasticity (min.)				
	0	4	6	8	10
Control (heated)	2.25	2.45	3.22	4.52	6.40
+0.1 per cent. Copper	1.71	1.82	3.21	4.40	5.98
+0.2 per cent. Copper	1.60	1.62	3.05	4.42	5.42
+0.3 per cent. Copper	1.50	1.69	3.00	4.40	5.70
+0.4 per cent. Copper	1.40	1.64	3.08	4.18	5.70

In a further experiment 0.1 per cent of copper powder was incorporated into a batch of raw rubber, which was then cut into small pieces about one square inch in area and one eighth of an inch thick, and placed inside a steam-jacketed air-oven into which air under pressure could be passed. The rubber was heated for 2 hours at 287° F, under an air pressure of 40 lb. per sq. in. The very tacky rubber obtained in this way was sheeted on a mixing mill, curing ingredients were added, and determinations carried out on the mixed rubber in the usual way.

TABLE 9

Copper	Plasticity (min.)					
	0	2	4	6	8	10
0.1 per cent	1.20	1.20	1.75	3.20	5.14	5.60

Both results (Tables 8 and 9) show that, although the presence of copper powder in small quantities brings about depolymerization and softening of the rubber, it does not act as a catalytic carrier of atomic oxygen to any appreciable

degree. On the evidence of these experiments showing the dissimilarity in behavior of rubbers oxidized with hydrogen peroxide and with molecular oxygen in the presence of copper as a catalyst, it would appear that copper, in the dark, does not act as a potent oxidizing agent towards an uncured rubber mixing of the composition specified. The failure of copper to act as a strong oxidizing catalyst towards an uncured rubber is in agreement with earlier results obtained by the author with copper and some of its salts and a quality of rubber somewhat similar to that used in these experiments.

TABLE 10

Copper salt	Increase in weight after 32 months aging (per cent)	
	Uncured	Cured 60 min. at 274° F
Precipitated copper powder	0.42	2.39
Cuprous chloride	0.41	2.24
Cupric chloride	0.41	2.82
Cuprous sulfide	0.35	2.28
Cupric sulfide	0.34	2.48
Copper carbonate	0.30	2.50
Copper nitrate	0.38	2.52
Copper chromate	0.30	1.99
Copper cyanide	0.32	2.38
Copper ferrocyanide	0.30	2.59

The decided increase in oxidation shown (Table 10) in the vulcanized samples of rubber seems to point to the rubber being depolymerized only in the uncured state, permitting oxidation to occur at a later stage under more favorable conditions as, for example, during the vulcanizing process.

Summarizing briefly, it would appear that retardation of the rate of set-up caused by excessive mastication of a rubber mixing is caused mainly by one factor in the process, that is, by the action of oxygen in its atomic form on the rubber. An attempt to reconstruct the catalytic action which is assumed to occur during the oxidizing process by using copper as the catalyst was not successful, and from these experiments it is concluded that copper in uncured rubber acts as an accelerator of depolymerization and not of oxidation.

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## HARDNESS TESTING OF VULCANIZED ELASTOMERS \*

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This report summarizes the various types of hardness determinations used for vulcanized elastomers. The chart is handy for conversions of hardness values obtained from one type of instrument to another.

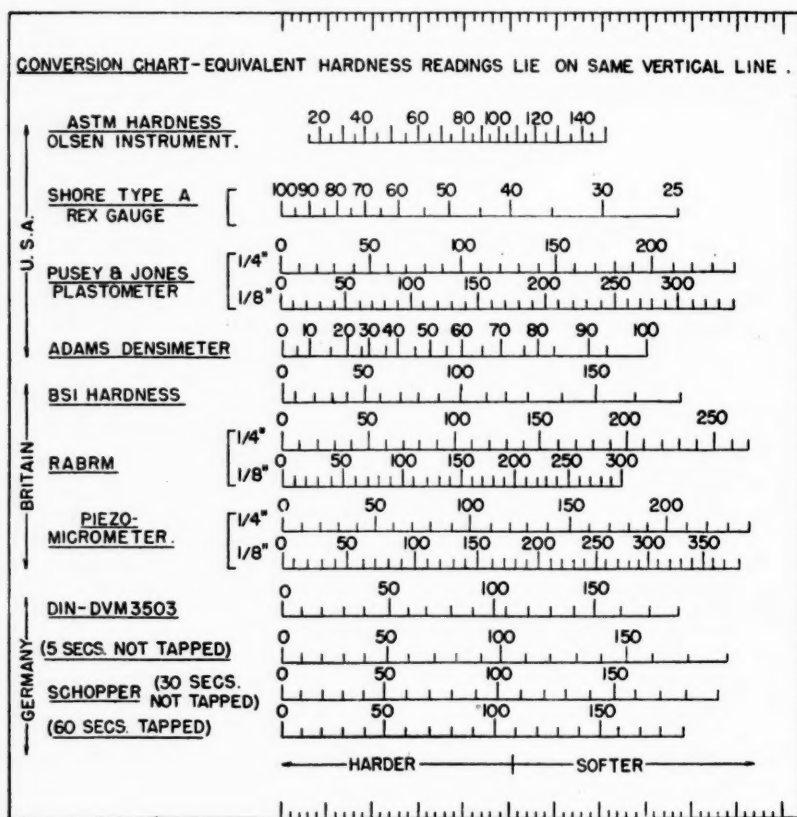


Fig. 1

The various types of instruments used to determine hardness can be divided into two classes:

I. Instruments operating under constant load. The majority of instruments fall in this class.

\* This is a transcript of blue sheet Report BL-185 of the Rubber Chemicals Division of E. I. du Pont de Nemours & Co., dated December 15, 1944.



II. Instruments operating with a spring. These are the simplest to operate and are pocket-size instruments.

In both cases hardness is determined by the depth to which a definite-shaped body dents the vulcanizate under a controlled load.

#### CLASS I. HARDNESS TESTERS OPERATING UNDER A CONSTANT LOAD

The various types which fall under this classification are described below:

A. *ASTM Hardness Tester*. (See ASTM Designation D314-39) (1) (12). This apparatus is also known as the Olsen Hardness Tester. The apparatus and test-specimens conform to the following conditions:

*Indenter*: Sphere—0.0938-inch diameter.

*Zero Load*: None.

*Test Load*: 5 pounds.

*Reading*: In 0.001 inch, 30 seconds after application of load.

*Dimensions of Test-Piece*: Minimum—0.5 inch thick and 2 inches lateral. In routine testing, other dimensions may be used.

*Test Temperature*: To be recorded and constant for a series of tests.

B. *Pusey and Jones Plastometer*. (See ASTM Designation D531-41) (1) (13).

The apparatus and test-specimens conform to the following conditions:

*Indenter*: Ball—1/8-inch diameter. For soft specimens a 1/4-inch ball may be used.

*Zero Reading*: Lower indenter shaft until contact is made with specimen and gauge-needle has made 3 revolutions. Dial shall then be adjusted to read zero.

*Zero Load*: Approximately 85 grams.

*Test Load*: 1000 grams.

*Reading*: In 0.01 mm., 1 minute after load is applied.

*Dimensions of Test-Piece*: 0.5 inch thick, 1.25 inches wide, 3 inches long. In routine testing other dimensions may be used.

*Test Temperature*: To be recorded and constant for a series of tests.

C. *BSI (British Standards Institution) Hardness Tester*. (2) (3) (11).

The apparatus and test-specimens conform to the following conditions:

*Indenter*: Ball—3/32-inch diameter.

*Zero Load*: 30 grams, applied for 5 seconds before application of full load.

*Test Load*: 535 grams (total load 565 grams).

*Reading*: In 0.01 mm., 30 seconds after application of load. Apparatus to be gently vibrated during this period to overcome friction.

*Thickness of Test-Piece*: Preferably 1 cm.

*Test Temperature*:  $21 \pm 3^\circ \text{C}$ .

D. *RABRM (Research Association of British Rubber Manufacturers) Hardness Gauge*. (4) (5).

The apparatus and test-specimens conform to the following conditions:

*Indenter*: Ball—1/8-inch or 1/4-inch diameter.

*Zero Load*: Negligible.

*Test Load*: 1000 grams.

*Reading*: In 0.01 mm., 1 minute after application of load. Apparatus to be gently tapped during this period.

*Dimensions of Test-Piece*: About 45 mm., diameter and 9 mm. thickness.

*Test Temperature*: Room temperature.

*E. Strachan Piezo-Micrometer.* (5) (6).

Very similar in principle and method of use to the Pusey and Jones Plastometer. The reading is also in 0.01 mm.

*F. Schopper Hardness Tester.* (5) (14).

The apparatus and test-specimens conform to the following conditions:

*Indenter:* Ball—10-mm. diameter.

*Zero Load:* Negligible.

*Test Load:* 1000 grams.

*Reading:* In 0.01 mm., 5 seconds and 30 seconds after application of load, without tapping. The chart shows readings made 60 seconds after application of the load and while the instrument was gently tapped.

*Dimensions of Test-Piece:* Same as described under RABRM Hardness gauge.

*Test Temperature:* Room temperature.

*G. DIN (German Standards Institution). Softness Gauge.* (7) (8) (11).

The apparatus and test-specimens conform to the following conditions:

*Indenter:* Ball—10-mm. diameter.

*Zero Load:* 50 grams.

*Test Load:* 1000 grams (total load 1050 grams).

*Reading:* In 0.01 mm., 10 seconds after application of load.

*Thickness of Test-Piece:*  $6 \pm 0.2$  mm.

*Test Temperature:*  $20 \pm 2^\circ \text{C}$ .

## CLASS II. HARDNESS TESTERS OPERATING WITH A SPRING

The various types which fall under this classification are as follows:

*A. Shore Durometer Type A.* (1) (15).

For description and operation of this apparatus, see ASTM Designation D676-42T. Other types of Shore durometers are available. They have the same construction and differ mainly from type A in that the spring of indentation is either firmer or weaker so that more accurate readings can be taken with vulcanizates of very high (hard rubber) or very low (sponge rubber) hardness. No readings with these instruments are shown in this report.

*B. Adams Densimeter.* (9).

This apparatus is very similar to the Shore Durometer. The scale is reversed so that low readings mean high hardnesses and *vice versa*. The instrument is used mostly by roller manufacturers for stocks of higher hardness ranges.

*C. Rex Hardness Tester.* (10).

This is a new instrument having the form and dimensions of a small fountain pen. It has a Vernier type of scale only, which gives optimum hardness readings. The values obtained with the Rex duplicate the maximum hardness readings obtained with a Shore Type A Durometer.

The data shown on the conversion chart should not be considered too exact. Hardness readings may vary with individual instrument, operator, temperature, and drift of the stock tested.

Hardness readings with BSI tester, RABRM gauge, Strachan Piezo-Micrometer, Schopper Tester, DIN gauge were assembled from various publications (see Bibliography). Readings with the other instruments were compiled from our Rubber Laboratory files.

Natural-rubber compounds were used in all instances.

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- <sup>7</sup> DIN Softness Designation DVM-3503, June, 1938. The DIN specifications can be obtained through "Beuth-Vertrieb GmbH", or "Deutscher Normenausschuss EV", both Berlin, Germany.
- <sup>8</sup> Kosten, *VDI Zeitschrift*, Vol. 86, page 536, 1942.
- <sup>9</sup> The Adams Densimeter is manufactured by Stowe-Woodward, Inc., Newton Upper Falls, Massachusetts.
- <sup>10</sup> The Rex hardness tester is manufactured by the Rex Gauge Co., Chicago, Illinois. Its sale is handled by the Naugatuck Chemical Division, U. S. Rubber Co., 1230 Sixth Ave., New York 20, N. Y.
- <sup>11</sup> Copies of foreign standards can often be obtained through the American Standards Association, 29 West 39th Street, New York, N. Y.
- <sup>12</sup> The Olsen hardness gauge is manufactured by the Tinius Olsen Testing Machine Co., 500 North 12th Street, Philadelphia, Pennsylvania.
- <sup>13</sup> The plastometer is manufactured by the Pusey and Jones Corp., Wilmington, Delaware.
- <sup>14</sup> The Schopper tester is manufactured by Louis Schopper, Leipzig, Germany.
- <sup>15</sup> The Shore Durometer is manufactured by the Shore Instrument & Mfg. Co., 90-25 Van Wyck Avenue, Jamaica, N. Y.

# SWELLING OF SYNTHETIC RUBBERS IN MINERAL OILS

## EFFECT OF TEMPERATURE AND ANILINE POINT \*

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Several methods have been suggested to measure the tendency of mineral oils to swell synthetic rubber compositions. The aniline point<sup>1</sup> of the oils has proved to be a simple and reliable index. It has already been adopted by two engineering societies<sup>2</sup> and by several private companies as a specification for mineral oils which may come in contact with synthetic rubber compositions.

This study was made to include oils with low aniline points and to measure swelling at different temperatures. Volatile hydrocarbons, an aromatic fuel blend, and kerosene were included in the list of swelling liquids. Since the earlier studies, American-made acrylonitrile-butadiene copolymers have become available, and two such rubbers were used in this study.

Four oil-resistant synthetic rubbers, Neoprene-GN, Stanco Perbunan, Hycar OR-15, and Thiokol-FA were compounded with about 28 volumes of SRF carbon black, using no extractable softeners. Thus the swelling values of these compounds are comparable. The compounds are shown in Table I.

TABLE I  
SYNTHETIC RUBBER COMPOSITIONS

Neoprene-GN (GR-M)	100	....	....	....
Stanco Perbunan	....	100	....	....
Hycar OR-15	....	....	100	....
Thiokol-FA	....	....	....	100
Stearic acid	0.5	0.5	0.5	0.5
Zinc oxide	5.0	5.0	5.0	10.0
Sulfur	....	2.0	1.5	....
Light magnesium oxide	4	....	....	....
Benzothiazyl disulfide	....	1.5	1.5	0.3
Diphenylguanidine	....	....	....	0.1
SRF (Gastex)	40	50	50	37.5
Sp. gr. of polymers	1.25	0.97	1.00	1.34
Sp. gr. of compound	1.41	1.19	1.22	1.51
Vol. black/100 vol. polymer	27.8	27.0	27.8	27.9
Vol. polymer/100 vol. compound	77.2	76.6	76.3	76.3

The compounds were cured as 0.075-inch slabs for 40 minutes at 300° F. The Thiokol compound was allowed to cool in the press.

Four oils were chosen as swelling liquids to cover a wide range of solvent powers, from a highly paraffinic oil to a mineral oil of lowest aniline point yet found. Kerosene and 40 per cent aromatic fuel blend, similar to PPF 813 fuel, were selected as representing the range of swelling likely to be encountered in volatile hydrocarbons. The properties of these oils are shown in Table II.

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 37, No. 1, pages 64-67, January 1945.

TABLE II  
SWELLING LIQUIDS

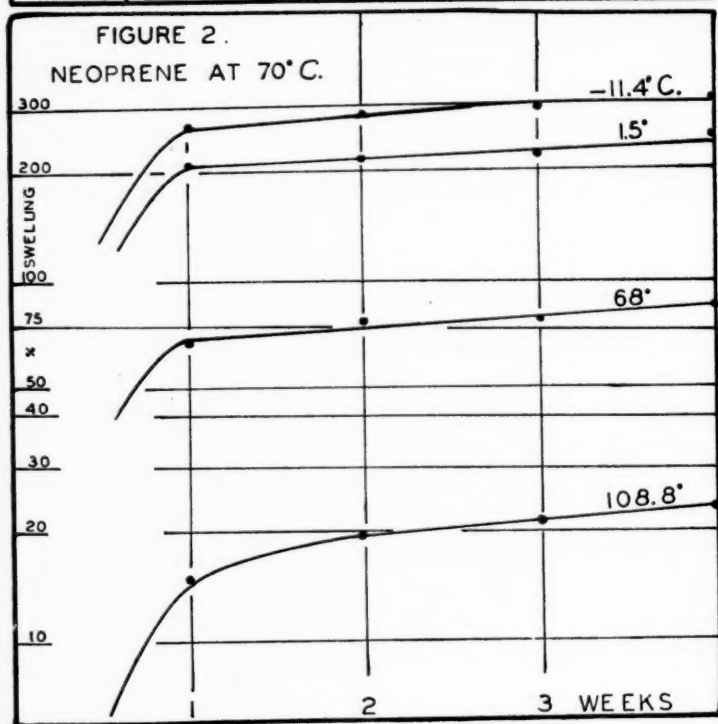
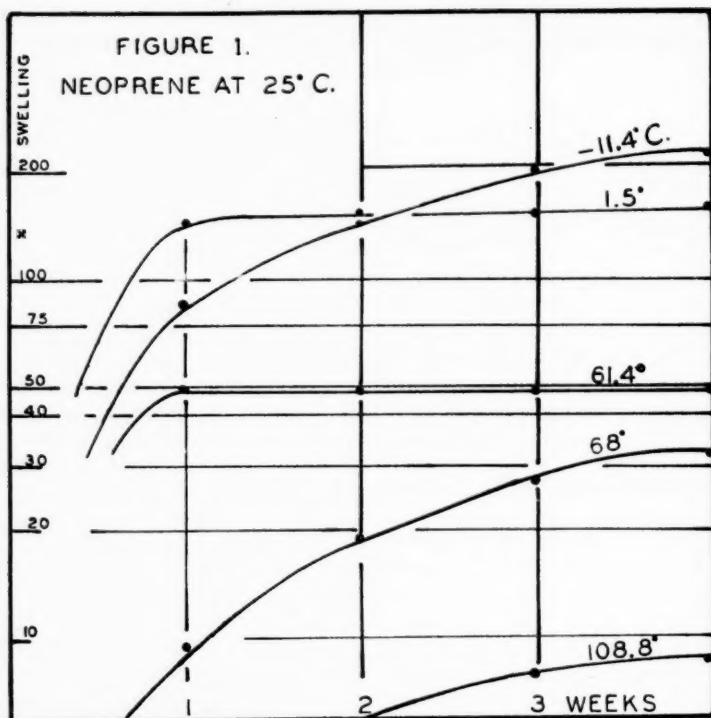
Type of Oil	Specific Gravity at 20° C	Saybolt Universal Viscosity at 37.8° C	Distillation Range		-50% Aniline Point, (° C)
			5%	95%	
SAE 30 motor	0.8806	455	..	...	108.8
White	0.8810	210	..	...	104.0
Plasticizing	0.9156	160	..	...	68.0
Kerosene	0.7545	...	88	257	61.4
Aromatic fuel blend	0.7685	...	60	140	1.5
Plasticizing	1.040	136	..	...	-11.4

The aniline point was determined at 50 per cent by weight. The usual methods<sup>3</sup> specify determination at 50 per cent by volume, but the mixture can be more accurately made by weighing<sup>1</sup> the aniline and oil. The difference in aniline point by the two methods is not great in most cases. Recently the monomethylaniline point<sup>4</sup> has been suggested as a measure of the swelling tendency. Since this value for petroleum lubricating oils is approximately 77° C below the aniline point, it is evident that it can be used in the same manner to predict the swelling of such petroleum products. Duplicate samples of each compound, 1 × 2 × 0.075 inch, were placed in separate jars at 25°, 70°, and 100° C. The volume change was measured by the displacement method<sup>5</sup> and hardness by the Shore durometer after 1, 2, 3, and 4 weeks of immersion.

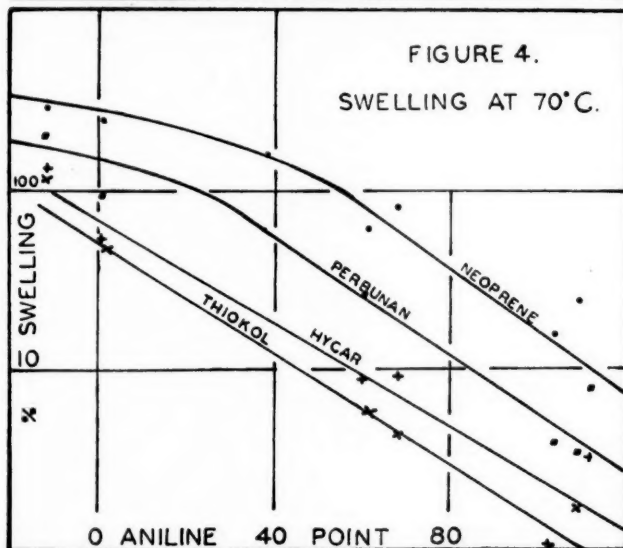
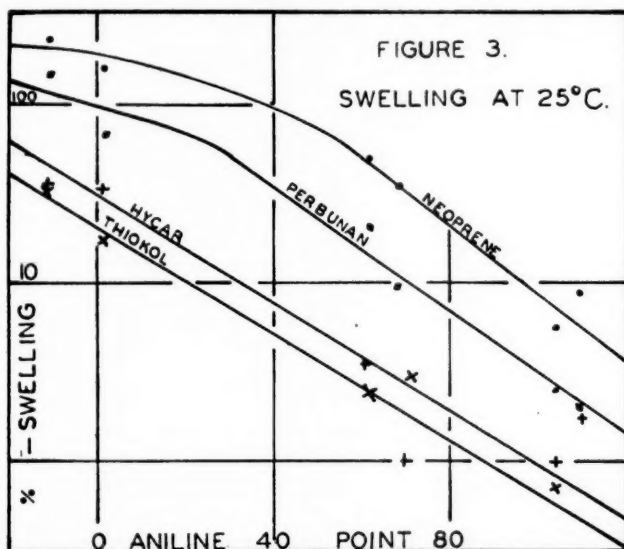
Dumbbells, cut to 0.25 × 1 inch in the restricted portion, were also placed in each liquid and were tested after 4 weeks of immersion. Tests were made in the swollen condition<sup>5</sup> before the volatile materials could evaporate. A Scott tester was used at 20 inches pull per minute. The immersed samples were conditioned at 70° F, and tested at the same temperature.

#### SWELLING RESULTS

The time-swelling curves of the Neoprene-GN compositions at 25° and 70° C are shown in Figures 1 and 2. The numbers on the curves refer to the aniline points of the oils. These curves are typical of compositions of other synthetics and show that, with low aniline-point oils, equilibrium may not be reached in 4 weeks at 25° C. With the less viscous volatile oils, equilibrium is reached in 1 to 2 weeks. The swelling at 25° C in the -11.5° C aniline-point plasticizing oil may be slightly below the equilibrium value. At 70° and 100° C equilibrium is reached in less than 4 weeks, and a slight decrease following the maximum swelling is noted in some instances. This effect was previously observed<sup>6</sup> and may be due to further curing of the sample. It is planned to study the effect of the degree of cure on the amount of swelling encountered. The results of the swelling tests at 25° C are shown in Figure 3. With each compound the logarithm of swelling varies inversely with the aniline point of the swelling liquid up to 100 per cent swelling. Hanson<sup>7</sup> had previously suggested from the results with one oil that the swelling of Neoprene-GN was not linear above 100 per cent; our results confirm this opinion. In most cases compounds which swell to this degree in service are of questionable utility. As noted above, the compounds showing a high degree of swelling at 25° C may not have reached equilibrium, but it does not appear that equilibrium swelling (Figure 1) would be enough greater to make the relation between aniline point and swelling linear.



The swelling tests at 70° C are shown in Figure 4. The compositions all had a greater degree of swelling than at 25° C; the synthetic rubbers are arranged in the same relative order, Neoprene-GN showing the greatest swelling, and Stanco Perbunan, Hycar OR-15, and Thiokol-FA progressively less swell-



ing. The aniline point varies inversely with the logarithm of swelling up to 100 per cent volume increase. At 100° C the volatile hydrocarbons were not used. The results of this temperature are shown in Figure 5; Thiokol is not included since the compounds were badly softened under conditions of test, and Thiokol is not usually recommended for service at this temperature.





The equations of the flat portion of the curves (Figures 3, 4, and 5) were derived to be as follows:

$$\text{Neoprene: } \log S = 2.75 + \frac{t}{146} - \frac{\text{A. Pt.}}{50}$$

$$\text{Perbunan: } \log S = 2.10 + \frac{t}{182} - \frac{\text{A. Pt.}}{58}$$

$$\text{Hycar: } \log S = 1.40 + \frac{t}{125} - \frac{\text{A. Pt.}}{58}$$

$$\text{Thiokol: } \log S = 1.18 + \frac{t}{113} - \frac{\text{A. Pt.}}{60}$$

where

$S$  = % volume increase

$t$  = temperature, °C

A. Pt. = 50% aniline point of oil

These equations must be regarded as a first approximation, but it is believed significant that the effect of a change of aniline point has the same effect on the logarithm of swelling, regardless of temperature. A decrease of 50° C in the aniline point of the oil gives ten times the swelling in the case of Neoprene-GN, within the linear portions of the curves; with Perbunan and Hycar compounds the value is 58° C, and with the Thiokol compound it is 60° C. The temperature coefficient seems to be somewhat larger with the compounds which exhibit less swelling.

The results with the Neoprene-GN composition were compared with the reported values of Fraser<sup>8</sup>, and of Hanson<sup>7</sup> and an earlier study<sup>1</sup> from this laboratory (A-70 and B-70). These results are shown in Figure 6. Hanson used the maximum aniline point in his figures, but his results have been re-drawn using the 50 per cent aniline point. Since these compounds have various amounts of filler and other compounding ingredients and since the conditions of cure vary somewhat, it is not surprising that the curves do not always coincide.

It is surprising that the slope of the curves is so nearly the same in almost every instance. This is in agreement with the finding above that the slope of the curve was independent of temperature, but also indicates that it is apparently independent of loading and normal variations of the degree of cure.

#### PROPERTIES OF SWOLLEN SAMPLES

Tensile test-pieces were immersed in the various liquids for 4 weeks, and tensile strength and hardness were determined in the swollen condition (Table III). The tensile strength is computed on the dimensions of the unswollen sample to make the results more nearly comparable. It will be noted that the volatile swelling liquids generally reduce the tensile strength for a given amount of swelling much more than the nonvolatile oils.

Low molecular-weight plasticizers usually have a greater softening effect than those with high molecular weights. Fraser<sup>9</sup> showed that volatile materials soon evaporate from Neoprene-GN, and that the tensile strength reaches that of the unswollen composition.

The tensile strength and elongation are not adversely affected by moderate

TABLE III  
PROPERTIES OF SWOLLEN COMPOSITIONS

Temp. (° C)	A. Pt. of Oil (° C)	Neoprene-GN				Perbunan			
		Swelling (%)	Tensile strength	Elonga- tion (%)	Shore hardness	Swelling (%)	Tensile strength	Elonga- tion (%)	Shore hardness
...	...	...	2870	370	69	...	2840	360	63
25	108.8	9.2	2890	390	66	2.2	2940	400	65
...	104	5.6	2860	430	67	2.5	2820	350	65
...	68	32.8	2460	440	60	9.0	2660	340	62
...	61.4	48.6	1750	250	56	19.6	1980	290	56
...	1.5	160.7	990	200	43	64.6	1230	180	50
...	-11.4	231.6	810	120	44	140.4	1310	180	44
70	108.8	23.8	2640	320	57	8.6	2980	340	63
...	104	16.2	2720	400	64	4.0	2280	250	66
...	68	81.9	1840	380	49	19.3	2620	350	59
...	61.4	62.2	1340	260	45	26.8	1520	220	55
...	1.5	244.2	580	180	33	94.6	920	170	46
...	-11.4	300.6	750	150	35	213.4	1290	170	45
100	108.8	32.0	770	130	55	8.6	2120	220	64
...	104	18.4	1670	120	65	5.6	2480	120	70
...	68	115.4	720	360	35	23.2	1420	140	61
...	-11.4	419.2	500	140	18	287.0	740	140	27
Temp. (° C)	A. Pt. of Oil (° C)	Hycar OR-15				Thiokol-FA			
		Swelling (%)	Tensile strength	Elonga- tion (%)	Shore hardness	Swelling (%)	Tensile strength	Elonga- tion (%)	Shore hardness
...	...	...	2960	400	70	...	920	470	60
25	108.8	2.3	2940	340	72	2.1	940	400	60
...	104	0	2940	320	72	1.0	920	450	60
...	68	1.0	2860	340	71	3.0	830	420	60
...	61.4	3.4	2860	400	69	2.3	820	420	59
...	1.5	34.4	1510	230	56	16.6	620	380	49
...	-11.4	35.4	2200	300	60	33.8	450	280	42
70	108.8	4.3	3060	320	72	1.8	800	320	61
...	104	0.8	2680	300	74	-0.6	840	330	62
...	68	9.0	3270	400	69	4.2	820	360	57
...	61.4	8.6	3020	310	65	5.5	610	280	55
...	1.5	49.6	1200	200	54	47.7	190	200	33
...	-11.4	145.8	1460	220	48	131.8	a	a	a
100	108.8	3.3	2660	210	76	-11.8	280	60	60
...	104	0.6	2420	140	80	-7.4	a	a	80
...	68	8.1	2310	170	70	-3.6	a	a	70
...	-11.4	167.2	1060	220	34	a	a	a	a

<sup>a</sup> Too weak to test

swelling, but as swelling approaches 100 per cent, the values show an appreciable decrease.

The hardness decreases in most instances with increased swelling, but there is a noticeable increase in some of the Perbunan and Hycar samples at 100° C. This suggests further vulcanization under the conditions of test.

### CONCLUSIONS

The aniline point of hydrocarbon oils and solvents is a satisfactory index of the swelling of oil resistant synthetic rubber compositions. The logarithm of the percentage volume increase varies inversely with the aniline point up to 100 per cent swelling. The slope of the swelling curve is apparently characteristic of each synthetic rubber, and is not affected by loading, temperature or degree of cure. Slight swelling does not greatly decrease the tensile strength, but above 100 per cent swelling the strength is greatly reduced.

### ACKNOWLEDGMENT

The authors wish to thank S. W. Eby for obtaining the swelling data and for determining the physical properties.

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# COMPARISON OF METHODS OF EXAMINING THE SCORCHING OF RUBBER STOCKS \*

J. F. MORLEY, J. R. SCOTT, AND W. H. WILLOTT

## INTRODUCTION

The experiments here described form a comparison of two well-known methods of examining the scorching of rubber stocks, namely, by the determination of plasticity<sup>1</sup> and by the determination of solubility in benzene<sup>2</sup>. The former has hitherto been the more widely used, but the latter is so much quicker and simpler, that if it is equally reliable, it might well replace the plasticity method for most purposes. It had been intended to include a third method, which consists in determining the period of time required for a solution of the stock to gel when heated<sup>3</sup>. The experiments by this method, however, were not a success and it was therefore abandoned.

## EXPERIMENTAL

### 1. METHODS

The stocks were prepared on a 6 in.  $\times$  12 in. experimental mill under the standard conditions adopted in the Laboratories of the Research Association of British Rubber Manufacturers. Part of each stock was sheeted out 15 mm. thick for the plasticity tests and part 1 mm. thick for the solubility tests. The sheets were dusted with zinc stearate and allowed to stand for 24 hours.

Two types of scorching treatment were applied:—(a) The test-pieces, prepared as described below, were dusted with zinc stearate and placed in test-tubes, which were then immersed in boiling water for various periods. The tubes were thereafter allowed to stand for 16 hours at room temperature and the specimens removed (it was found that if the tubes and specimens were dusted with zinc stearate before heating, the specimens could easily be removed). (b) The specimens, contained in test-tubes, were heated for 30 minutes at various temperatures in a glycerin bath, and thereafter allowed to stand for 16 hours at room temperature. (Note: Examination of the test results, especially for Series II, shows that the temperature attained by the stock in method (a) must have been lower by some 30° C than in the 100° C tests by method (b). As the exact temperature of the stock was not determined in either method, and the difference is immaterial to the purpose of the investigation, the nominal figure of 100° C has been used throughout).

The methods used for examining the degree of scorching were as follows.

*Plasticity method.*—The specimens used were substantially cylindrical pieces of 2 cc. volume, prepared by cutting a cylinder about 14 mm. diameter from the 15 mm. sheet with a sharp cork-borer and trimming off the edges with scissors until the correct weight was obtained. For the plasticity test the specimen was preheated for 15 minutes and then compressed in a parallel-plate (Williams) plastimeter under 5 kg. load, thickness readings being taken after various periods. The preheating and test temperature was 70° C.

\* Reprinted from the *Journal of Rubber Research*, Vol. 13, No. 12, pages 168-176, December 1944.

**Solubility method.**—Pieces  $25 \times 3$  mm. cut from the 1 mm. sheet were used as the specimens. The degree of scorching was examined by pouring about 5 cc. of benzene into the tube containing the specimen, allowing to stand for 1 hour at room temperature, and shaking. By this treatment unscorched samples partially dissolve, rendering the liquid cloudy or opaque, whilst scorched samples merely swell and leave the benzene clear.

**Gelling method.**—An attempt was made to test the scorching of the second series, A–K (see section 3 below) by observing the time required for a xylene solution of the stock to gel when kept at  $100^\circ\text{C}$ . It was found, however, that if the amount of xylene used was such as would give a reasonably fluid solution in all cases, no gelling occurred after several hours at  $100^\circ\text{C}$ . The method was therefore abandoned as being unsuitable for normal technical work.

## 2. SERIES I: PRELIMINARY EXPERIMENTS

Tests were made with the following mixings:

	A	B	C
Rubber	100	100	100
Sulfur	2.5	2	3
Whiting	—	—	75
Zinc oxide	5	5	5
Stearic acid	1	1	1
Mercaptobenzothiazole	0.75	—	—
Tetramethylthiuram disulfide	—	0.25	0.25

For A and B batches containing 600 g. of rubber were prepared; 400 grams was used for C.

The complete test results are given in Tables 1–4.

TABLE 1  
PLASTICITY RESULTS: SPECIMENS HEATED AT  $100^\circ\text{C}$

Period of heating (min.)	Thickness (mm./100) after compression for (minutes)									
	0.25	0.5	0.75	1	2	3	4	5	6	10
<i>Mix A</i>										
0	323	280	258	238	211	195	184	176	170	154
30	330	285	265	250	218	202	190	182	177	160
60	320	280	—	244	216	200	189	180	175	166
90	320	280	260	245	215	200	188	180	174	159
97	330	290	268	252	221	205	195	187	179	165
105	330	290	270	251	221	205	195	187	180	165
112	340	295	274	260	230	213	203	194	188	172
120	340	298	280	266	236	221	210	203	196	180
150	416	384	363	350	322	305	295	288	282	268
<i>Mix B</i>										
0	318	272	251	231	204	187	177	169	163	148
30	305	268	248	232	205	190	180	172	167	152
37	340	296	—	263	233	219	208	201	195	178
45	340	303	280	268	237	221	212	205	198	181
52	380	340	—	310	—	280	264	257	248	230
60	465	440	424	412	390	379	370	365	361	352
<i>Mix C</i>										
0	315	271	251	235	206	187	176	168	161	145
30	298	264	241	229	199	183	173	165	159	145
37	315	270	—	230	202	186	175	167	161	146
45	325	278	260	244	211	194	184	175	169	153
52	303	272	255	245	222	209	200	194	189	177
60	382	350	329	320	290	278	270	262	258	249

TABLE 2  
PLASTICITY RESULTS: SPECIMENS HEATED FOR 30  
MINUTES AT VARIOUS TEMPERATURES

Temperature, °C	Thickness (mm./100) after compression for (minutes)										
	0.25	0.5	0.75	1	2	3	4	5	6	8	10
<i>Mix A</i>											
unheated	323	280	258	238	211	195	184	176	170	161	154
100	327	285	262	248	225	198	186	177	171	161	155
105	345	300	275	260	225	209	199	190	185	175	169
110	340	295	270	255	222	206	195	185	179	170	163
115	500	460	440	425	390	370	356	348	339	329	320
<i>Mix B</i>											
unheated	318	272	251	231	204	187	177	169	163	155	148
90	325	275	252	232	201	183	172	165	160	151	145
95	345	300	278	263	228	212	200	193	188	178	172
105	430	—	385	370	340	325	315	306	301	292	286
110	—	930	—	—	—	—	—	—	—	—	—
<i>Mix C</i>											
unheated	315	271	251	235	206	187	176	168	161	152	145
90	315	270	246	230	200	183	172	165	159	150	144
95	325	272	245	230	198	180	170	162	157	148	142
105	290	265	240	225	198	184	174	167	162	154	147
110	—	950	—	—	—	—	—	—	—	—	—

TABLE 3  
SOLUBILITY TEST: SPECIMENS HEATED AT 100° C

Period of heating (min.)	Mix A	Mix B	Mix C
15	soluble	soluble	soluble
30	soluble	soluble	soluble
45	soluble	soluble	soluble
60	soluble	insoluble	soluble
75	soluble	insoluble	soluble
90	soluble	insoluble	insoluble
120	soluble	—	—
150	soluble	—	—
180	soluble	—	—
210	soluble	—	—

TABLE 4  
SOLUBILITY TEST: SPECIMENS HEATED FOR 30 MINUTES  
AT VARIOUS TEMPERATURES

Temperature (°C)	Mix A	Mix B	Mix C
90	—	soluble	—
95	—	soluble	—
100	soluble	—	—
105	soluble	slightly soluble	soluble
110	soluble	insoluble	soluble
115	soluble	—	—

Three out of the four tests, namely those in Tables 1, 2, and 3, agree in placing the mixes in the following order: A (least scorching), C, B (most scorching); the other test, Table 4, likewise shows B to scorch most readily, but does not enable A and C to be differentiated.

There is thus qualitative agreement between the plasticity and solubility methods in indicating the relative tendencies of different mixes to scorch.



To obtain a quantitative comparison it is necessary to adopt some definition of scorching time as determined by the plasticity method. For practical purposes this may be regarded as the period of time which produces just enough scorching to make the stock troublesome in processing. According to Odewald and Baader<sup>4</sup> an increase of about 40 per cent in "deformation hardness" represents definite scorching, which would lead to trouble, for instance, in extruding. From the theory of parallel-plate plastimetry<sup>5</sup> and the known plastic properties of rubber stocks<sup>6</sup>, it can be shown that 1 per cent difference in deformation hardness should correspond to a change in thickness, after 10 minutes' compression under 5 kilograms of the order of 0.3 per cent. Definite scorching should thus correspond to about 12 per cent increase in this thickness. The period of heating required to increase the 10-minute plasticity figure by 12 per cent has therefore been taken as the scorching time. The reason for adopting the 10-minute reading will be explained later. In determining the scorching time, the plasticity figures were plotted against period of heating and a smooth curve was drawn through the points so as to minimize the effects of experimental errors.

In the solubility method the scorching time is taken as the mean of the longest period that leaves the stock soluble and the shortest that renders it insoluble, or alternatively as the period that renders the stock slightly soluble. Analogous definitions are adopted for the scorching temperature in the tests at various temperatures. The scorching times and temperatures so obtained are shown in Table 5.

TABLE 5

	Scorching time at 100° C	
	Plasticity method	Solubility method
Mix A	112 min.	>210 min.
Mix B	35 min.	52 min.
Mix C	50 min.	82 min.
	Scorching temperature	
Mix A	109° C	>115° C
Mix B	94° C	105° C
Mix C	106° C	>110° C

In the determinations of scorching time at 100° C, both forms of test agree in placing C much nearer to B than to A; a similar comparison between the methods is not possible in the case of scorching temperature.

According to these results the solubility method appears less sensitive than the plasticity method, because a longer heating period or higher temperature is required to render the stock insoluble in benzene than to produce definite scorching according to the plasticity test.

In using the plasticity method attention must be given to the choice of the best period of compression, *i.e.*, that which shows the effect of scorching soonest and/or gives the most sensitive indication of the change in plasticity produced by scorching. From an examination of the present data there is no evidence that any particular period has a marked advantage in giving an earlier indication of scorching than another; if anything, the advantage seems to lie with the longer periods.

The most sensitive indication of scorching is given by that compression period for which the increase in the plasticity figure is greatest in relation to the error of measurement. The increase in the plasticity figure during the early

stages of scorching is about the same for all periods of compression, but the error of measurement decreases considerably as the period is lengthened; thus, in the present experiments, the average difference between duplicate tests is as follows.

Period of compression (min.)	Difference in plasticity figure (mm./100)
0.25	9
0.5	6
0.75	4
1	5
2	4
3	2.5
4	2.2
5	2.2
6	2.0
8	2.0
10	1.8

A relatively long period, such as 10 minutes, is therefore preferable; a still longer period would probably be even better.

### 3. SERIES II: FULLER COMPARISON OF THE PLASTICITY AND SOLUBILITY METHODS

The object of this series was to see how nearly the two methods would place different stocks in the same order as regards scorching tendency. Accordingly, ten mixings of the following compositions were examined.

	A	B	C	D	E	F	G	H	J	K
Rubber	100	40	100	100	100	100	100	100	100	100
Whole-tire reclaim	—	100	—	—	—	—	—	—	—	—
Sulfur	2.5	2.5	3.0	2.5	2.5	3.0	2.0	2.0	2.0	2.0
Antimony sulfide*	—	—	—	5	5	—	—	—	—	—
Barytes	—	—	—	40	40	—	—	—	—	—
Clay (Devolite)	—	—	—	—	—	—	—	50	—	—
Gas black	—	—	—	—	—	38	—	—	—	—
Magnesium carbonate	—	—	—	—	—	—	—	—	—	50
Whiting	—	—	75	—	—	—	—	—	—	—
Zinc oxide	5	5	5	5	5	7.5	5	5	75	5
Petroleum jelly	—	—	—	—	—	—	—	4	—	2
Pine tar	—	3	—	—	—	2	—	—	—	—
Stearic acid	1	—	1	1	1	2	—	—	3	2
Butyric dehydianiline (Vulcafor-BA)	0.75	0.75	—	—	—	—	—	—	—	—
Mercaptobenzothiazole	—	—	—	—	0.75	0.75	—	—	—	—
Tetramethylthiuram disulfide	—	—	0.25	—	—	—	—	—	—	—
Vulcafor-DAU	—	—	—	0.4	—	—	—	—	—	—
Zinc diethyldithiocarbamate	—	—	—	—	—	—	0.4	0.5	—	—
Zinc pentamethylenedithiocarbamate	—	—	—	—	—	—	—	—	0.4	0.4

\* Golden, no calcium sulfate or free sulfur.

In each case the batch mixed was 5 times the formula weight, in grams. The test procedure was exactly the same as in Series I except that the  $25 \times 3 \times 1$  mm. specimens for the solubility tests were cut from the thickly sheeted stock, instead of from stock separately sheeted to 1 mm. thickness, so as to avoid differences in milling treatment between the plasticity and solubility specimens.

As the 10-minute plasticity reading has been shown above to be preferable, the tabulated results (Tables 6 and 7) have been limited to this reading together with the 0.5-minute and 3-minute readings to give some indication of the form of the time-compression curve.

The scorching periods and scorching temperatures, deduced as described in Series I, are given in Table 10. With some stocks the plasticity reading de-

creases slightly before scorching starts; in these cases the 12 per cent increase taken to denote scorching has been reckoned from the lowest point of the time/plasticity curve. The fact that results are given in some cases to the nearest minute or degree C does not imply that the results are believed to be accurate to this degree. Results in brackets are approximate estimates only.

TABLE 6  
PLASTICITY RESULTS (THICKNESS OF SPECIMEN, MM./100).  
SPECIMENS HEATED AT 100° C

Period of compression (min.)	Period of heating (min.)											
	0	10	20	30	40	50	60	75	90	105	125	160
<i>Mix A</i>												
0.5	416	—	—	402	425	421	446	466	551	650	747	891
3	305	—	—	300	310	318	332	365	455	559	679	842
10	244	—	—	244	252	263	273	315	402	502	623	792
<i>Mix B</i>												
0.5	293	—	—	370	469	440	488	513	578	623	672	795
3	230	—	—	317	420	385	437	465	531	572	620	740
10	200	—	—	284	387	348	407	430	495	530	576	694
<i>Mix C</i>												
0.5	357	—	—	337	338	337	332	341	358	466	520	920
3	255	—	—	236	237	238	233	246	272	386	453	896
10	205	—	—	189	190	193	189	200	228	351	419	879
<i>Mix D</i>												
0.5	380	380	427	472	522	572	642	—	—	—	—	—
3	272	278	335	388	438	498	558	—	—	—	—	—
10	218	227	286	348	397	458	518	—	—	—	—	—
<i>Mix E</i>												
0.5	457	—	—	481	537	583	765	889	939	987	1019	1030
3	335	—	—	364	427	487	693	838	904	951	992	1001
10	270	—	—	309	372	436	645	796	879	928	974	985
<i>Mix F</i>												
0.5	451	—	—	464	455	446	461	503	494	484	504	523
3	340	—	—	352	349	345	357	377	385	374	398	410
10	291	—	—	306	306	302	316	334	345	331	353	363
<i>Mix G</i>												
0.5	300	291	307	363	711	974	—	—	—	—	—	—
3	207	199	211	266	653	956	—	—	—	—	—	—
10	165	157	169	223	616	943	—	—	—	—	—	—
<i>Mix H</i>												
0.5	343	326	321	336	358	522	797	—	—	—	—	—
3	237	225	225	236	265	433	742	—	—	—	—	—
10	187	178	180	193	222	395	712	—	—	—	—	—
<i>Mix J</i>												
0.5	361	358	435	628	1000	—	—	—	—	—	—	—
3	254	252	341	544	957	—	—	—	—	—	—	—
10	203	203	301	507	929	—	—	—	—	—	—	—
<i>Mix K</i>												
0.5	350	358	423	737	897	954	940	—	—	—	—	—
3	254	254	330	674	858	919	913	—	—	—	—	—
10	203	203	283	633	827	886	887	—	—	—	—	—

TABLE 7

PLASTICITY RESULTS (THICKNESS OF SPECIMEN, MM./100). SPECIMENS HEATED FOR 30 MIN. AT VARIOUS TEMPERATURES

Period of compression (min.)	Temperature of heating (° C)						
	Unheated	90	95	100	105	110	115
<i>Mix A</i>							
0.5	416	—	412	412	414	476	535
3	305	—	304	303	338	381	444
10	244	—	245	246	291	330	394
<i>Mix B</i>							
0.5	293	—	432	453	565	655	694
3	230	—	368	386	500	600	638
10	200	—	332	351	458	555	590
<i>Mix C</i>							
0.5	357	—	345	308	350	320	467
3	255	—	243	211	248	227	380
10	205	—	196	178	205	188	345
<i>Mix D</i>							
0.5	380	429	463	483	668	690	660
3	272	333	365	406	593	614	588
10	218	285	318	372	550	586	546
0.5	457	—	487	635	969	—	—
3	335	—	368	532	928	—	—
10	270	—	310	477	898	—	—
<i>Mix F</i>							
0.5	451	—	500	448	436	450	474
3	340	—	367	348	340	354	385
10	291	—	315	305	301	316	348
<i>Mix G</i>							
0.5	300	317	560	774	806	—	—
3	207	216	461	742	800	—	—
10	165	171	421	716	788	—	—
<i>Mix H</i>							
0.5	343	325	323	530	—	—	—
3	237	225	227	440	—	—	—
10	187	180	182	394	—	—	—
<i>Mix J</i>							
0.5	361	796	994	—	—	—	—
3	254	703	931	—	—	—	—
10	203	656	886	—	—	—	—
<i>Mix K</i>							
0.5	350	447	720	—	—	—	—
10	254	346	628	957	—	—	—
10	203	293	563	913	—	—	—

The plasticity method always gives a shorter scorching time, that is, an earlier indication of scorching, than the solubility method, the average difference being 9 minutes. Usually, also, the plasticity method indicates a lower scorching temperature, the difference averaging 5° C. These differences in time and in temperature vary from one mix to another, but this appears to be due largely to experimental error, since a large difference in scorching time is not necessarily accompanied by a large difference in scorching temperature.

TABLE 8  
SOLUBILITY TEST: SPECIMENS HEATED AT 100° C

Mix	Period of heating (min.)											
	0	10	20	30	40	50	60	75	90	105	125	150
A	S	—	—	S	S	S	S	(s)	I	I	I	I
B	S	—	—	(v)	I	I	I	I	I	I	I	I
C	S	—	—	S	S	S	S	S	(s)	I	I	I
D	S	S	S	(s)	I	I	I	—	—	—	—	—
E	S	—	—	S	(v)	I	I	I	I	I	I	I
F	I	—	—	I	I	I	I	I	I	I	I	I
G	S	S	S	I	I	I	I	—	—	—	—	—
H	S	S	S	S	(s)	(v)	I	—	—	—	—	—
J	S	S	(s)	I	I	I	I	—	—	—	—	—
K	S	S	(s)	I	I	I	I	—	—	—	—	—

S = soluble; (s) = slightly soluble; (v) = very slightly soluble; I = insoluble.

TABLE 9  
SOLUBILITY TEST: SPECIMENS HEATED FOR 30 MIN. AT VARIOUS TEMPERATURES

Mix	Temperature of heating (° C)						
	Unheated	90	95	100	105	110	115
A	S	—	S	(s)	(s)	(s)	I
B	S	—	I	I	I	I	I
C	S	—	S	S	S	S	I
D	S	S	S	(s)	I	I	I
E	S	—	S	S	I	I	I
F	I	—	I	I	I	I	I
G	S	(s)	(s)	I	I	—	—
H	S	S	S	S	I	I	I
J	S	(s)	I	I	—	—	—
K	S	(s)	(s)	I	I	—	—

TABLE 10

Mix	Scorching period (min. at 100° C)		Scorching temperature (° C for 30 min. heating)	
	Plasticity method	Solubility method	Plasticity method	Solubility method
A	59	75	103	105
B	(17)	30	<95(?90)	<95
C	85	90	113	113
D	14	30	<90(?87)	100
E	28	40	95	103
F	75	*	112	*
G	22	25	90	93
H	34	45	97	103
J	14	20	<90†	90
K	17	20	(88)	93

\* No estimate possible because the unheated stock did not dissolve.

† Apparently considerably below 90° C.

The results of this series of experiments agree with those of Series I in showing that the plasticity method detects a rather earlier stage of scorching than does the solubility method, although the differences between results given by the two methods are smaller than in Series I. There is good agreement between the orders in which the mixings are arranged by the two methods of test, as is shown by Table 11; disagreements are found only in the upper part of the Table where scorching is very rapid and the errors of measurement, at least for scorching time, relatively large.

If the scorching times given by the two methods are plotted one against the other, the correlation is seen to be so close as to leave no doubt that the methods measure essentially the same property; the same is found, though not in quite so striking a fashion, with the scorching temperatures. This close correlation is confirmed by a calculation of the correlation coefficient which is highly significant in both cases. Table 11 shows also that scorching time and

TABLE 11

	Scorching time		Scorching temperature		
	Plasticity method	Solubility method	Plasticity method	Solubility method	
Shortest	D, J K, (B) G E H A F C	J, K G B, D E H A — C	D, J K G, (B) E H A F C	J, (B) G, K D — E, H A — C	Lowest
Longest					Highest

scorching temperature arrange the mixings in closely similar orders, as would be anticipated. The relationship between these two quantities is such that an increase of  $10^{\circ}\text{C}$  in the scorching temperature, *i.e.*, the temperature that produces scorching in a given period corresponds approximately to a doubling of the scorching time, *i.e.*, the period required to produce scorching at a given temperature. This indicates that scorching has a factorial temperature coefficient of about 2.0 per  $10^{\circ}\text{C}$ , which is of the same order as the temperature coefficient of vulcanization, as would be expected.

The failure of Mix F to dissolve in benzene even before heating is presumably due to its fairly large content of gas black, since it is known<sup>7</sup> that very finely dispersed fillers render unvulcanized rubber stocks difficultly soluble. This fact represents a limitation to the usefulness of the solubility method of examining scorching. It may be noted that the results for Mix D in Table 10 confirm a previous observation that even a delayed-action accelerator may induce rapid scorching in presence of antimony sulfide.

#### 4. SERIES III: SOLUBILITY METHOD USING DIFFERENT SOLVENTS

According to the results of Series I and II, scorching is not made evident as early by the benzene-solubility test as by a plasticity test. A less powerful solvent than benzene might, however, indicate a less advanced degree of scorching and so give results similar to those of the plasticity method. A series of tests was accordingly made, with a mixing of the same composition as C in the second series, to compare the results obtained by using benzene, petroleum ether (b.p.  $40^{\circ}\text{--}60^{\circ}\text{C}$ , density 0.65 at  $25^{\circ}\text{C}$ ), diethyl ether, and cyclohexanone (Sextone) as solvents. The results are given in Tables 12-14.

Benzene, petroleum ether, and diethyl ether give substantially the same results, which, somewhat unexpectedly, in this case agree more or less closely with those of the plasticity method. When cyclohexanone is used, the normal criterion of scorching obviously cannot be applied, since the unheated stock is only slightly soluble. If complete insolubility (I in Table 13) is taken as the criterion, the scorching time is indicated as 60 minutes and the scorching temperature as  $110^{\circ}\text{C}$ . The former is shorter than the times indicated by all the other methods (Table 14), but the temperature is about the same. According

TABLE 12  
PLASTICITY RESULTS (THICKNESS OF SPECIMEN, MM./100)

Period of compression (min.)	Specimens heated at 100° C for (min.)						
	0	30	45	60	75	90	120
0.5	339	316	312	303	327	656	1350
3	245	225	218	214	231	620	1340
10	198	184	176	172	189	593	1333
	Specimens heated for 30 min. at (° C)						
	Unheated	100	105	110	115	120	
0.5	339	316	310	310	354	1015	
3	245	225	221	217	261	1003	
10	198	184	179	176	218	988	

TABLE 13  
SOLUBILITY TESTS

Solvent	Specimens heated at 100° C for (min.)						
	0	30	45	60	75	90	120
Benzene	S	S	S	S	(s)	I	I
Petroleum ether	S	S	S	S	(s)	I	I
Diethyl ether	S	S	S	S	(s)	I	I
Cyclohexanone	(s)	(s)	(v)	I	I	I	I
	Specimens heated for 30 min. at (° C)						
	Unheated	105	110	115	120		
Benzene	S	S	(s)	I	I		
Petroleum ether	S	S	(s)	I	I		
Diethyl ether	S	S	S	I	I		
Cyclohexanone	(s)	(v)	I	I	I		

(Abbreviations as in Table 8)

TABLE 14

Solvent	Scorching period (min.)		Scorching temperature (° C)	
	Plasticity method	Solubility method	Plasticity method	Solubility method
	75	—	113	—
Benzene	—	75	—	110
Petroleum ether	—	75	—	110
Diethyl ether	—	75	—	112
Cyclohexanone	—	?	—	?

to these tests, therefore, none of the alternative solvents examined shows any marked advantage over benzene. A wider search among the available organic solvents might, however, reveal one combining the advantages of good solvent power for the unscorched rubber and early indication of the onset of scorching.

#### SUMMARY AND CONCLUSIONS

A comparison has been made between the plasticity and solubility methods of examining the scorching of accelerated rubber stocks; trials with a third method, based on the gelling of a solution of the stock, were unsuccessful.

In a comparison using 10 different stocks the plasticity and solubility methods arranged these in practically the same order as regards tendency to scorch, showing that the two methods measure essentially the same property.



The plasticity method usually detects an earlier stage of scorching than the solubility method using benzene as the solvent. Attempts to improve the sensitiveness of the latter method by using a less powerful solvent did not give promising results, as petroleum ether and diethyl ether behaved very similarly to benzene, while cyclohexanone did not readily dissolve the unscorched stock.

The solubility method is unsuitable for stocks containing considerable percentages of gas black, *e.g.*, tire tread stocks, and presumably also for those containing other strongly reinforcing fillers, because the unscorched stock does not dissolve in benzene.

In determining the period for which a stock can be kept at a given temperature, or the temperature at which it can be kept for a given period, without practically serious scorching taking place, the plasticity method is to be preferred on account of its greater sensitiveness. It has the further advantage of giving a quantitative measure of the degree of scorching. However, for purely comparative purposes (but excluding stocks of the type referred to in 4 above) the solubility method is just as reliable, and has the advantage of being much simpler and quicker. By this method, also, it would usually be possible to decide whether any given piece of stock were scorched or not, whereas by the plasticity method this could not be done unless an unscorched piece of the same stock was available for comparison.

In using the parallel-plate plastimeter for scorching tests, a relative long period of compression (10 minutes or more) gives the most sensitive indication of the change in plasticity produced by scorching.

In the stocks examined the rate of scorching is, on the average, approximately doubled by a temperature rise of 10° C.

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